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A HORIZONTAL A.C. ARC AS SPECTRUM EXCITATION SOURCE FOR ORES AND MINERALS

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Spectral analysis is widely used for the analysis of ores and minerals which are non-homogeneous and are non-conducting. The universal spectrum excitation source in these cases is the carbon arc, which can be relied on to ensure evaporation of all materials known to us and to get the spectrum of most of the elements.

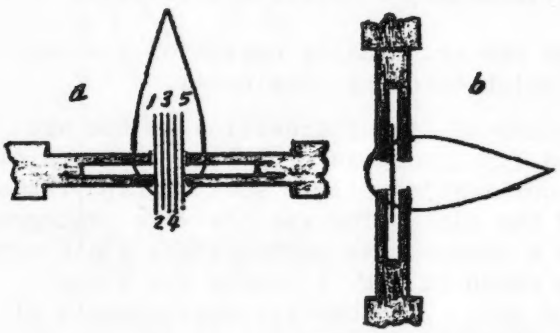

Fig. 1. Position of the arc flame reflection on the spectrograph slit when photographing spectra.

Quantitative analysis of ores and minerals, however, often present a difficult problem. The main reason for this is the fractional evaporation of elements, which is accompanied during evaporation of the test sample by concentration changes of the elements in the gas cloud round the arc and by changes in temperature of the arc flame [1]. This results in changes in the line intensity during the burning of the arc which are related to the composition of test material. One must also remember that the position of the arc flame itself is not usually characterized by its constancy with respect to the electrodes, and this in turn leads to an irregular behavior of the constancy of line intensity because of uneven element concentration distribution and irregular gas cloud temperature.

In the analysis of ores and minerals, therefore, it is of great importance to find conditions for test sample evaporation and arc burning conditions which will decrease the effect of fractional evaporation and also ensure a stable position for the arc flame; if this can be effected, conditions can also be so arranged that a flame is obtained, different parts of which differ considerably from each other in temperature and also in the concentration of the elements contained in it.

This will enable one to use those parts of the flame for which illumination of the lines of the test elements is optimal. These conditions are satisfied to some extent by simultaneous evaporation of the sample from two horizontally disposed A.C. carbon arc electrodes. When this arrangement of the elec-

trodes is adopted, a stable tongue of flame which is directed upward is formed, occupying the position shown in Fig. 1, a with respect to the electrodes.

According to our observations, the stability of the flame can be increased considerably by addition of compounds of elements with low ionization potentials to the test powders, since they favor the stabilization of the temperature of the arc flame during their evaporation.

Satisfactory results were obtained, e.g., by diluting the ore in a ratio of 1:2 to 1:5 with a mixture of 5 parts strontium sulfate and 8 parts of spectrographically pure graphite powder, and using sharpened carbon electrodes 8 mm long and 3 mm in diameter with openings 2 mm in diameter drilled in them. Sharpening of the electrodes and drilling of the holes were carried out with a special cutter and took 10-20 seconds.

When the arc was supplied with A.C. (15 A, 220 V, arc gap 4 mm), there was fairly regular intake of strontium into the arc flame, which coincides with the intake of the majority of the elements found in the middle of the volatility series for the elements given below [2].

The Intake Sequence of the Elements in the Arc Flame during Evaporation of Oxides from the Carbon Electrode Channel

Li,Na,K,Rb,Cs

(Hg,As,Cd,Zn,Bi,Sb,B,Pb,Tl,Mo,Sn,W), (Mn,Mg,Cu,Ge,In,Ga)

Rare earths

(Fe,Co,Ni,Ba,Sr,Ca,Si,Be,Al,V,Cr,Ti,U,Se,Mo,Re,Zr,Hf,Th,Nb,Ta,W,B)

One should note that the burning of the arc usually ceases of its own accord after evaporation of the sample, which takes ca. 2 minutes.

In order to determine the distribution of line intensities in the arc flame the image of the latter, decreased 1.3 times, was projected by means of a quartz lens on to the slit of an autocollimating Hilger spectrograph fitted with an antivignetting lens in front of the slit. The spectra were photographed in the course of 1 minute 30 seconds on a diapositive photographic plate with contrast factor of 1.6 in the positions shown in Fig. 1,a for the flame image with respect to the spectrographic slit. Photometric measurements of the spectral lines obtained for these positions of the flame allow one to deduce the distribution of the line intensity in various parts of the flame on going from bottom to top of the flame.[1)]

In order to get information about changes in line intensity in the part of the flame along the electrode axis, the spectra were photographed by turning the image of the flame through 90° (Fig. 1,b).

Rotation of the flame image is effected by means of the quartz prism set up in front of the slit, using total internal reflection obtained by the parallel position of the prism base in relation to the pencil of light.

The spectra were photographed in all cases through a net of parallel filaments fixed in front of the spectrograph slit; this ensured the appearance of longitudinal bright lines at equal distances from each other on the spectrogram. This enables one to determine easily to which part of the arc flame the various parts of the spectral line photographed correspond. The trans-

---

1) I. V. Ilyasova took part in the work of getting spectrograms and establishing the distribution of line intensities in the arc cloud.

formation from the blackening values found for the different parts of the lines to their intensity was carried out by the usual method of using the characteristic curves of the photographic plate, the background of the spectra being taken into account.

By finding the distribution of the line intensity in the part of the flame between the electrodes, it is possible to control changes in the absolute value of the line intensities when getting spectra in other positions of the flame, and to express their line intensities in all cases on one scale. Lines for which the phenomenon of self-absorption were not observed were measured.

A study of the distribution of line intensities in the arc flame showed that when an A.C. arc is used, there is always obsefved a clearly expressed increase for both arc and spark lines near the electrodes, which is common to all the elements. This increase occurs independently of the ionization potential and atomic weight of the elements and of the volatility of the material of which the test element is a component.

As examples, we have adduced in Fig. 2 the characteristic changes in line intensity in the flame on going from one electrode to the other along the axis for the lines V I 3185.4, V II 3110.7, Be II 3131.1, Be I 2650.8 and Ba I 3071.6. These curves are the evaporation curves of quartz containing 0.03% of vanadium

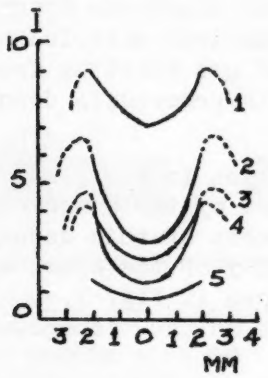

Fig. 2. Change in line intensity along the electrode axis. A.C. arc 220 V, 15 A. 1 – Be II 3131.1; 2 – V I 3185.4; 3 – V II 3110.7; 4 – Ba I 3071.6; 5 – Be I 2650.8.

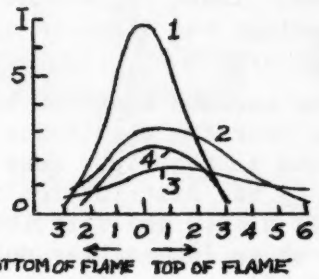

Fig. 3. Change in line intensity along the length of the flame. A.C. arc 220 V, 15 A. 1 – Be II 3131.1; 2 – V I 3185.4; 3 – Ba I 3071.6; 4 – V II 3110.7.

pentoxide, 0.02% beryllium oxide, and 0.5% barium oxide. Before the powders were placed in the electrode canals, they were diluted in the ratio 1:5 with a mixture of strontium sulfate and graphite.

The elements for which curves are adduced differ considerably both in ionization potentials (barium 5.2, vanadium 6.7, beryllium 9.3 eV) and in atomic weight (barium 137.4, vanadium 50.9, beryllium 9.0).

The transition from bottom to top of the flame is always accompanied by first, a regular increase, followed by a weakening in line intensity of the elements. The characteristic change in intensity for the vanadium, barium, and beryllium lines indicated above on passing through the center of the flame from bottom to top of the flame is shown in Fig. 3.

Fig. 4 depicts as an example, the change in the vanadium arc line of 3185.4 along the axis for the positions 1, 2, 3, 4, and 5 of Fig. 1, a, of the flame image on the spectrograph slit.

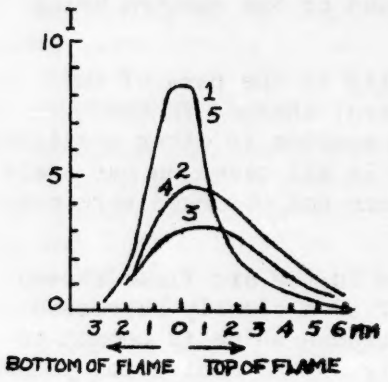

Fig. 4. Change in intensity of the V I 3185.4 line along the length of the flame for the positions of the flame indicated on Fig. 1,a.

A study of Fig. 4 shows that the greatest maxima are exhibited by the curves depicting the parts of the flame nearest the electrodes.

The regular character of the distribution of line intensities in an A.C. arc is shown up particularly clearly when curves are constructed which connect parts of the flame with equal line intensities; e.g., a study of Figs. 5 and 6 shows that the curves connecting the parts of equal intensity for the lines V I 3185.4 and V II 3110.7 and also Ba I 3071.6 and Be II 3131.1 are disposed symmetrically in the arc flame separating the regions of the flame with near values of line intensities. The transition on the drawings from one region of the flame to another is accompanied by a two-fold change in line intensity.

The regions of the arc flame radiating the lines of greatest intensity are always concentrated near the electrodes and touch the electrode channels, from which the gaseous products of the evaporation of the test material enter into the flame. These regions are reminiscent of jets of gas bursting from the electrode openings and directed upward by streams of air proceeding downward into the arc.

It can be assumed that the line intensity distribution in the parts of the arc flame near the electrodes is basically determined by the distribution of the elements in the vapor near the arc. The correctness of this assumption is borne out by the distribution of the relative intensity of the spark and arc lines V II 3110.7 and V I 3185.4 in the flame as shown in Fig. 7,a, the ratio of whose intensities depends to a large extent on the temperature of the arc flame [3].

In the central part of the flame the relative intensity of the lines indicated proved to be 0.7, while on passing into adjacent regions of the flame, this ratio was 0.6, 0.5, etc.

A comparison of Figs. 5, 6, and 7 shows that the distribution of line intensities of the elements in the flame does not agree with the distribution of the relative intensity of the vanadium lines, which indicates that in the central regions of the flame enclosed by the electrodes, no significant temperature changes were observed.

At the same time the distribution of the relative intensity of the spark and arc lines of vanadium shows that a transition from the center of the flame to its upper part should be accompanied by a regular temperature decrease, which undoubtedly should reflect on the intensity of the spectral lines. These conclusions were later confirmed by measuring the temperature and concentration of elements in various parts of the gas cloud round the arc.

The arc temperature was calculated from the ratio of intensities of the arc lines Bi 2938.32 and 2989.05 with known values of excitation energy and from the value of $A_{ik} \frac{g_1}{g_o}$ [4].

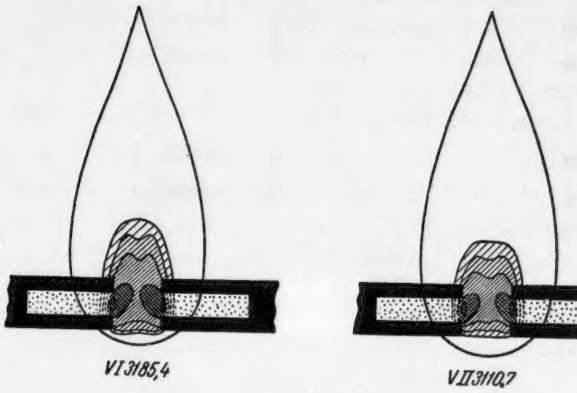

Fig. 5. Distribution of intensities of the lines V I 3185.4 and V II 3110.7 in the arc flame on evaporation of the test material from two electrodes. A.C. 20V, 15A.

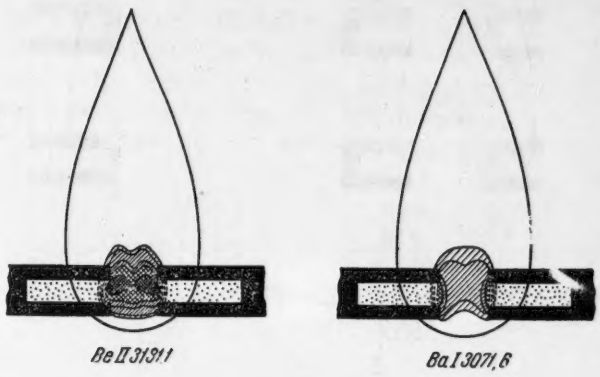

Fig. 6. Distribution of the intensities of the lines Be II 3131.1 and Ba I 3071,6 in the arc flame when the test material is evaporated from two electrodes. A.C. 220 V, 15 A.

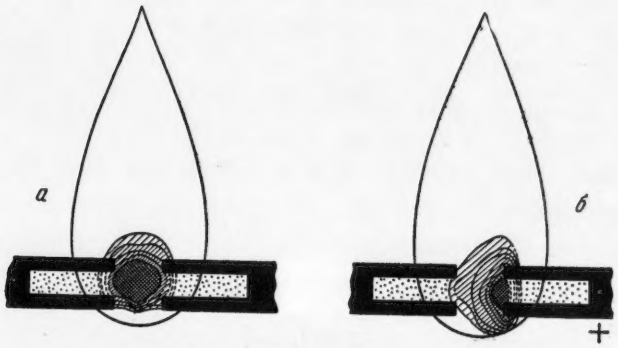

Fig. 7. Distribution of the relative intensity of the lines $\frac{\text{V II } 3110.7}{\text{V I } 3185.4}$ in the flame on evaporation of the test material from two electrodes. a) A.C. 220 V, 15 A; b) D.C. 180 V, 12 A.

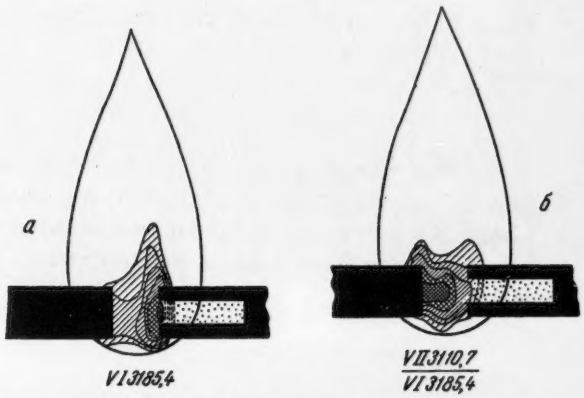

Fig. 11. Distribution of the intensity of the VI 3185.4 line and of the relative intensity of the lines $\frac{\text{V II } 3110.7}{\text{V I } 3185.4}$ in the arc flame on evaporation of test material from one electrode. A.C. 220 V, 15 A.

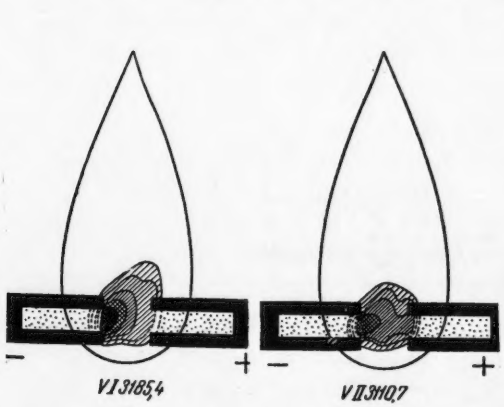

Fig. 13. Distribution of the line intensities of V I 3185.4 and V II 3110.7 in the arc flame on evaporation of test material from two electrodes. D.C. 180 V, 12 A.

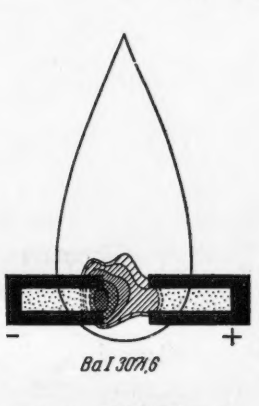

Fig. 14. Distribution of intensity of the line Ba I 3071.8 in the arc flame during evaporation of test material from two electrodes. D.C. 180 V, 12 A.

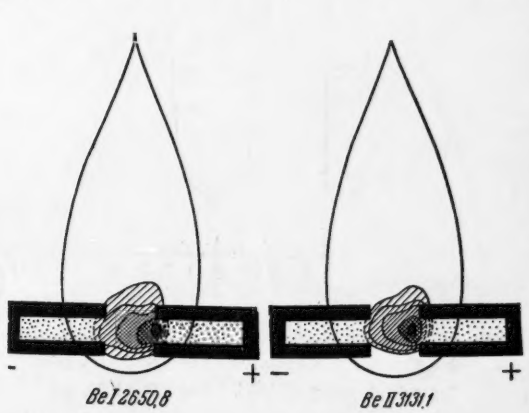

Fig. 15. Distribution of the intensities of the Be I 2650.8 and Be II 3131.1 lines in the arc flame during evaporation of test material from two electrodes. D.C. 180 V, 12 A.

The temperature was calculated by Ornshtein's method.

The high volatility of bismuth and its compounds excludesthe possibility of introducing bismuth into the flame by evaporation from the electrode canal. The introduction of bismuth into the arc was therefore realized by using the chloride and spraying this into the arc from below [5]. On setting up the sprayer under the arc the cloud formed by means of the pulverizer is sucked into the flame by the rising air stream.

When this method was employed, a small amount of bismuth regularly entered the flame (ca. 0.03 mg bismuth/minute) and the phenomenon of reabsorption was not observed for the bismuth line.

The results obtained showed that the temperature in the middle of the flame was 5300°K and changes to a comparatively small amount on going from the center of the flame to the electrodes. This agrees with the distribution of the relative line intensity of V II 3110.7 and V I 3185.4 observed previously.

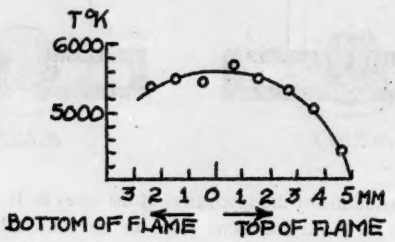

Fig. 8. Temperature change along the length of the flame. A.C. 220 V, 15 A.

The temperature distribution in the flame on going from bottom to top of the flame through its center as shown in Fig. 8, indicates that in this case there is a rapid fall in temperature. Thus at a height of 5 mm from the center of the arc, there is a temperature fall of 1400°K.

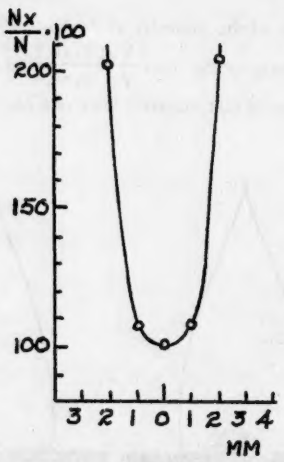

Fig. 9. Change in the relative concentration of vanadium atoms in the flame along the electrode axis. A.C. arc 220 V, 15 A.

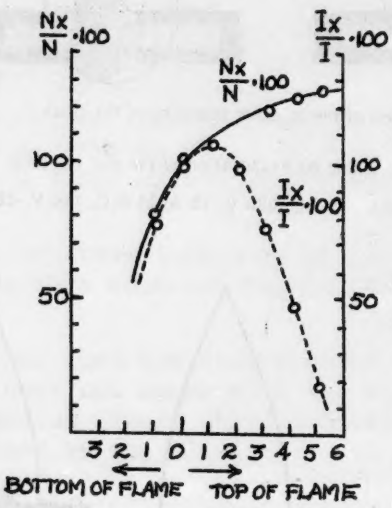

Fig. 10. Change in the relative concentration $\frac{N_x}{N} \cdot 100$ of vanadium atoms, and in the relative intensity $\frac{I_x}{I} \cdot 100$ of the V I 3185.4 line along the length of the flame. A.C. arc 220 V, 15 A.

By measuring the relative intensity of the arc lines 3185.4 of vanadium along their length and using the value of the arc temperature found, it is possible to calculate the distribution of the relative concentration of neutral

vanadium atoms in the arc flame. The following expression was used for calculating the relative concentration of vanadium atoms N_x/N:

$$\frac{N_x}{N} = \frac{I_x}{I} \cdot e^{-\frac{E}{K}\left(\frac{1}{T} - \frac{1}{T_x}\right)},$$

where I is the intensity of the vanadium line at the center of the arc; I_x is the intensity for other parts of the flame. The value of the excitation potential assumed for the V I 3185.4 line was 3.96 eV [6].

The distribution found for the relative concentration of vanadium atoms in the arc flame on going upward from the arc center and also from right to left in the direction of the electrodes is shown by the curves in Figs. 9 and 10.

At the same time the change in relative intensity of $\frac{I_x}{I}$ of the arc line of vanadium 3185.4 is shown in Fig. 10 for comparison.

On the basis of these diagrams, it is possible to conclude that the strengthening of the lines near the electrodes is accompanied by a considerable increase in concentration of neutral atoms, and consequently of the total concentration of elements near the electrode canals filled with the vapor of the test material. On going from the center of the arc to the end of the flame the maximal concentration of neutral atoms is only observed at a certain distance from the arc center. An explanation of this phenomenon is to be sought in the deviation of the gas streams errupting upward from the electrode canals, and a decrease in the extent of atomic ionization with fall in temperature.

The presence of intense bands of cyanide in the 3520-4220 A region of the carbon arc spectrum leads to overlapping of a series of the analytical lines of the elements. This is of particular importance, e.g., in the analysis of ores for their contents of indium, thallium, gallium, some of the rare earths, and also for strontium, barium, niobium, lead and other elements.

As our experiments showed, the fall in temperature on passing from the arc center to the end of the flame leads to a more rapid weakening of the cyanide bands in comparison with the analytical lines of a number of elements which usually possess low excitation potentials. This permits one, when carrying out an analysis, to choose those parts of the flame in which the lines of the test elements are not masked by cyanide bands.

By setting up two weak A.C. electro-magnets in a definite position under the arc, it is possible to change the shape of the flame as one wants, and at the same time extend the choice of the parts of the flame suitable for analysis. By regulating the current fed to the electro-magnets by means of a rheostat, it is possible, e.g., to force the flame to deviate downward or to occupy a position in the center between the electrodes.

Weakening of the cyanide band can be effected by addition of sodium carbonate instead of strontium sulfate to the ore. It should be noted, however, that the addition of sufficient of the volatile sodium carbonate to the ore led to a comparatively brief decrease in arc temperature. Consequently sodium carbonate can only be used for the analysis of elements which proceed from ore to arc flame at the same time as the sodium carbonate. These properties are exhibited by the elements which are found at the beginning, and in a bit of the middle of the volatility series adduced above for element oxides in the carbon arc.

Prolonged weakening of the cyanide bands and simultaneous stabilization of flame temperature can be achieved by the simple introduction of a cotton

wick with sodium carbonate, or a glass rod [8], into the arc flame from below.

Stabilization of arc temperature by the introduction of compounds of elements with low excitation potentials into one of the electrodes and evaporation of the test sample from the other electrode is of undoubted interest for the spectral analysis of ores and minerals. Unfortunately, in this case observation did not lead to positive results since the unsymmetrical evaporation of test material from the horizontally disposed electrodes caused an extremely uneven distribution of line intensities in the arc cloud. As an example, we have adduced in Fig. 11, a the distribution of intensities of the V I 3185.4 line on evaporation of the test material from the canal of one of the electrodes. It should be noted that evaporation of test material from one electrode also leads to a very significant change in excitation conditions on going from one part of the flame to another. Fig. 11, b corroborates this; here is shown the change in relative intensity of the lines V II 3110.7 and V I 3185.4.

As already indicated simultaneous evaporation of test sample in an A.C. arc from two horizontally disposed electrodes always leads to a symmetrical distribution of line intensities in the arc cloud which is practically independent of the composition of test sample and the properties of the elements. Replacement of A.C. by D.C. leads to a distribution of line intensities which is uneven and which also depends on test composition and properties of the elements. When D. C. is used the polarity of the electrodes is clearly manifest; this polarity destroys the concentration distribution of the elements in the arc cloud and leads to a strengthening near the cathode of elements with comparatively low ionization potentials [7]. The latter is known to take place as a result of the attraction of positively charged ions by the cathode, and consequently there is an increase in element concentration near the cathode.

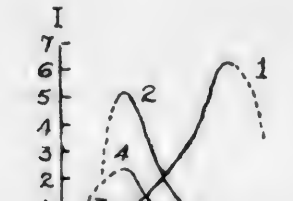

Fig. 12. Change in line intensity in the flame along the electrode axis. D.C. Arc 180 V, 12 A. 1 – Be II 3131.1; 2 – V I 3185.4; 3 – V II 3110.7; 4 – Ba I 3071.6

This strengthening of lines near the cathode was clearly observed, e.g., for the arc and spark lines of vanadium, and particularly for barium, which has a low value for the ionization potential (Fig. 12).

On the other hand, in the case of beryllium, which has a fairly high ionization potential, there was observed a strengthening of the lines near the anode. This can be explained on the grounds that the temperature of the anode is higher than the cathode, thus leading to a more rapid evaporation of material from the anode canal.

The overall picture of intensity distribution for the lines V I 3185.4, V II 3110.7, Be II 3131.1 and Ba I 3071.6 for a D.C. arc is illustrated in Figs. 13, 14, and 15.

The distribution of relative intensity of the V II 3110.7 and V I 3185.4 lines in the arc flame indicates non-uniformity of the excitation conditions in different parts of the D. C. arc (Fig. 7, b).

SUMMARY

1. A horizontal carbon arc between electrodes filled with test material is a valuable excitation source for ores and minerals.

2. The general uniformity of the symmetrical distribution of the intensi-

ties of arc and spark lines of elements in a horizontal A.C. arc has been demonstrated; this distribution is practically independent of the properties of the elements and of the volatility of the compounds.

3. It has been shown that the distribution of line intensities in a D.C. arc, in contrast to that in an A.C. arc, is of a complex nature and depends on the properties of the elements.

4. An explanation of the distribution line intensities in the arc flame has been given which is based on measurements of temperature distribution and of the distribution of the relative concentration of the atoms in the arc.

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ULTRAVIOLET COLORIMETRIC DETERMINATION OF SMALL AMOUNTS OF KETONES

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The methods which are most widely used at present for the quantitative determination of ketones have been worked out as a rule with an eye to the analysis of acetone. Their sensitivity varies within the limits 10^{-3} to 10^{-4} % acetone in the test material [1-6]. A nephelometric method of determining acetone proposed by Shikhvargen, according to the author, permits a quantitative determination of acetone to be made down to concentrations in solution of $5 \cdot 10^{-5}$ %.

In previous papers [7,8], we have observed that the application of the iodoform reaction, and subsequent colorimetric determination in the ultraviolet of the iodoform formed, during the reaction to the determination of acetone, methylethylketone, and methylpropylketone, enables the sensitivity of the quantitative determination of these ketones to be increased to $2 \cdot 10^{-5}$ %.

In the present paper, we give the results of a systematic investigation of the applicability of the method indicated to the quantitative analysis of aliphatic ketones. As test materials we used aqueous solutions of the following ketones: acetone, methylethylketone, pentanone-2, hexanone-2, heptanone-2, and octanone-2.

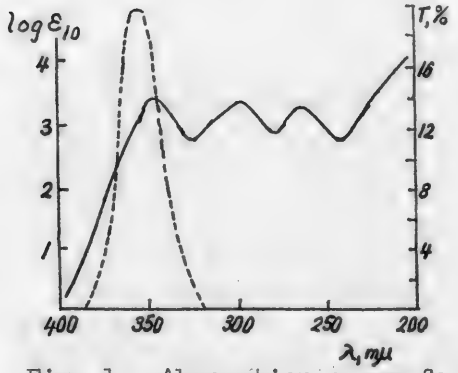

Fig. 1. Absorption curve for iodoform — full line; transmission curve for the light filter used — dotted line; T % — transmission of light filter in percentage; ϵ_{10} — molar absorption coefficient of iodoform.

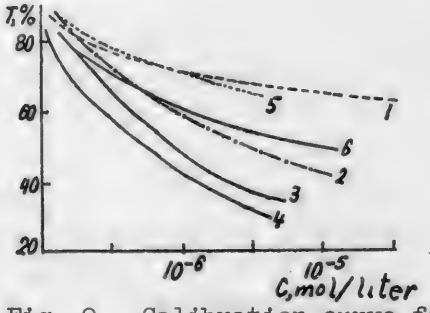

Fig. 2. Calibration curve for ketones.
1 — Acetone; 2 — Methylethylketone; 3 — Heptanone-2; 4 — Hexanone-2; 5 — Heptanone-2; 6 — Octanone-2; T % — Transmission of solutions in percentage; cuvette length — 2 cm.

All the ketones listed should give the iodoform reaction in accordance with the equation:

$$CH_3-CO-R + 3I_2 + 4NaOH = CHI_3 + R-COONa + 3NaI + 3H_2O.$$

In the course of this work we held to the following sequence of operations: 20 ml of iodine solution of the composition 200 g KI + 100 g I_2 + 400 ml H_2O was placed in a water-cooled separating funnel and 6.6 ml of 20% NaOH and 20 ml of test solution containing the test ketone added. The funnel was stoppered and shaken vigorously for 5 minutes, and excess iodine removed by addition of a few drops of 5% hyposulfite.

The iodoform which separated was extracted with 20 ml of pure chloroform (or with the same amount of ether dried over metallic sodium), the extract was transferred to a cylindrical cuvette provided with quartz windows, and the solution colorimetrically measured in the absorptiometer described by us previously [9].

TABLE 1

Weight of ketone taken, in %	Found, Δ in %	c/c %
Acetone		
0.00150	0.00150	0
0.00094	0.00093	1
0.00042	0.00041	2.5
0.00021	0.00020	5
0.000180	0.000186	3
0.000068	0.000070	3
0.000033	0.000035	8
Methylethylketone		
0.00173	0.00180	4
0.00067	0.00066	1.5
0.00040	0.00039	2.5
0.00025	0.00025	0
0.000173	0.000185	7
0.000069	0.000065	6
0.000032	0.000028	13
Methylpropylketone (pentanone-2)		
0.00177	0.00174	2
0.00130	0.00134	5
0.00042	0.00045	5
0.00022	0.00021	5
0.00015	0.00015	0
0.000075	0.000075	0
0.000040	0.000035	12
0.000018	0.000029	11

TABLE 2

Weight of ketone taken, in %	Found, Δ in %	c/c %
Methylbutylketone (hexanone-2)		
0.00205	0.00200	2.5
0.00102	0.00098	4
0.00078	0.00081	4
0.00025	0.00024	4
0.000110	0.000116	6
0.000076	0.000073	4
0.000042	0.000048	15
0.000021	0.000018	16
Methylamylketone (heptanone-2)		
0.00143	0.00137	4
0.00071	0.00067	6
0.00061	0.00058	5
0.00057	0.00060	6
0.00020	0.00020	0
0.00012	0.00014	17
0.000099	0.000105	5
Methylhexylketone (octanone-2)		
0.00090	0.00088	3
0.00063	0.00062	2
0.00055	0.00054	2
0.00038	0.00035	7
0.00025	0.00021	16
0.00016	0.00016	0

The iodoform absorption curve adduced in Fig. 1 shows that the greatest sensitivity of determination is achieved by carrying out colorimetric determination with a filter which isolates the spectrum at 360 mμ, since the absorption coefficient of iodoform in this region has a value of ca. 7000 cm^2/mol.

The transmission curve of the light filter used by us in the present work is adduced in Fig. 1 as the dotted curve.

Calibration curves for the ketones studied for a cuvette length of 2 cm are adduced in Fig. 2. Despite the fact that the time taken to carry out the iodoform reaction was varied from 5-20 minutes, we did not succeed in getting coincident curves, which suggests that there is a considerable difference in the rate of the iodoform reaction for ketones of different molecular weight.

Some of the results which were obtained during the analysis of ketone solutions are adduced in Tables 1 and 2. The rather large volume of the cuvettes we used did not permit us to cut down on the volume of liquid used for extraction of the iodoform. Despite this the sensitivity of determination was equal in some cases to twice that of Shikhvargen's nephelometric method. Increased length of cuvette and a smaller volume of extracting solvent should increase the sensitivity considerably, so that it should approximate to 10^{-6}% of ketone in the test mixture.

In parallel with the study of the sensitivity of colorimetric determination in the ultraviolet of aliphatic ketones, we also carried out some experiments on the analysis of mixtures of acetone with formaldehyde with the object of finding out the possibility of determining acetone colorimetrically in the presence of large amounts of the second component.

Some of the results obtained for mixtures of acetone and formaldehyde are given in Table 3. These results show that for a ratio of acetone to formaldehyde greater than 1:100, the concentration of acetone actually found was considerably lower than its real value. Up to this ratio, acetone was determined quantitatively with a relative error varying from 0 to 20%.

TABLE 3

Expt. No.	Amount of acetone taken in %	Amount of formaldehyde taken in %	Transmission of solution	Amount of acetone found in %	$\Delta c/c$ %
1	$3.97 \cdot 10^{-4}$	0	70	$3.97 \cdot 10^{-4}$	0
2	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-4}$	70	$3.97 \cdot 10^{-4}$	0
3	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-3}$	72.5	$3.50 \cdot 10^{-4}$	12
4	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-2}$	74	$3.15 \cdot 10^{-4}$	21
5	$3.97 \cdot 10^{-4}$	$4 \cdot 10^{-1}$	83	$2.40 \cdot 10^{-4}$	40
6	$3.97 \cdot 10^{-4}$	4	93.5	$0.7 \cdot 10^{-5}$	82

This systematic decrease in the concentration of acetone actually found in solution as compared with its true value which occurs when large amounts of formaldehyde are present is related probably to the formation of stable complexes between acetone and formaldehyde which do not readily undergo the iodoform reaction.

SUMMARY

1. It has been shown that it is possible to carry out quantitative analysis of aqueous solutions of acetone, methylethylketone, methylpropylketone, methylbutylketone, methylamylketone, and methylhexylketone by colorimetric determination in the ultraviolet using the iodoform reaction. The sensitivity is $2 \cdot 10^{-5}$%, the relative error 0-15%, and the time taken to make a determination 15-20 minutes.

2. It has been established that colorimetric determination of acetone in solution in the presence of formaldehyde is possible for ratios of acetone

to formaldehyde up to 1:100.

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1) See Consultants Bureau Translation, page 89.
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DETERMINATION OF BERYLLIUM IN BRONZE

BY MEANS OF A CATION EXCHANGE RESIN (CATIONITE)

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In order to get accurate results during beryllium determination, it is essential to separate it from many elements which accompany it, including aluminum and iron. Since, however, beryllium resembles aluminum in its chemical properties, separation from the other presents certain difficulties.

The following methods are in current use for the separation of beryllium from aluminum and iron; the acetate-tannin ortho-hydroxyquinoline method [1], the carbonate method, and also a method based on the difference in the hydrolytic properties of beryllium and aluminum succinates, respectively [2].

Many of the methods enumerated above take a long time to carry out, require expensive reagents and do not ensure the necessary accuracy. We set ourselves the task of finding a method which is free from these objections.

On the basis of preliminary experiments it was established that the easiest way of solving the problem was to separate beryllium from aluminum and iron chromatographically.

The basis of this separation of beryllium from aluminum and iron was their capacity to form complex compounds with oxalic acid according to the following equations:

$$AlCl_3 + 3H_2C_2O_4 = H_3[Al(C_2O_4)_3] + 3HCl;$$

$$FeCl_3 + 3H_2C_2O_4 = H_3[Fe(C_2O_4)_3] + 3HCl;$$

$$BeCl_2 + 2H_2C_2O_4 = H_2[Be(C_2O_4)_2] + 2HCl.$$

Although all these metals form complex oxalates, their respective oxalates differ considerably from each other in stability. Thus, the complex oxalates of aluminum and iron maintain the coordinate sphere in weakly acid solution (pH 4.4-5), while complex beryllium oxalate is stable in neutral or weakly alkaline solutions.

It is just this difference in the stability of the respective complex oxalates of bivalent beryllium and trivalent aluminum and iron which is a function of the pH that was used for their separation. The cation exchange resin used was SBS as before [3], 15 g of which was placed in a 100 ml buret and transformed into the hydrogen form before use. Initially an attempt was made to separate beryllium from aluminum and iron after their absorption by the cation exchange resin. This was carried out as follows: To the weakly acid solution containing beryllium, aluminum, and iron, ammonia was added until a turbidity appeared which was then removed by addition of a few drops of hydrochloric acid. The solution thus obtained was passed through a column at a rate of 2 ml/minute. Under these conditions, the ions of all these metals are absorbed by the cation exchange resin. The column was then eluted with 2% oxalic acid until all the aluminum and iron had been extracted; removal of all the iron was checked by testing with potassium thiocyanate. After removal of

aluminum and iron with oxalic acid, the beryllium was extracted from the cation exchange resin by passing through 10% hydrochloric acid. It was then precipitated in the filtrate with ammonia and determined gravimetrically. Results of determination of beryllium in solutions containing aluminum and iron are adduced in Table 1.

TABLE 1

Amount taken, in mg			Amount of Be found, in mg	
Be	Al	Fe		
9.2	1.3	2.2	8.6	9.1
			9.1	8.8
			8.9	9.0

Although satisfactory results were obtained for beryllium by this method, it cannot be applied for this purpose, because extraction of aluminum and iron from the cation exchange resin by oxalic acid is very slow. Another separation technique was therefore employed; aluminum and iron were complexed as oxalates before passing the original solution through the column. To the weakly acid solution containing beryllium, aluminum, and iron, was added a 2% solution of oxalic acid followed by ammonia dropwise until an alkaline reaction to methyl orange (pH 4.4) was obtained. This solution was then passed through a column at a rate of 2 ml/minute; when this was done, the aluminum and iron in the form of complex anions $[Me(C_2O_4)_3]^{3-}$ passed through into the filtrate while beryllium was absorbed on the cation exchange resin. After washing the column with distilled water, the beryllium was extracted from the cation exchange resin with 10% hydrochloric acid, and the beryllium finally determined gravimetrically as before. Results for the determination of beryllium in solution containing aluminum and iron by the second method are adduced in Table 2.

TABLE 2

Amount taken, in mg			Amount of Be found, in mg
Be	Al	Fe	
4.0	1.3	2.2	4.3; 3.9; 3.8
10.0	1.3	2.2	9.6; 10.0; 9.9
14.0	1.3	2.2	14.1; 13.8; 13.7

The results obtained for beryllium are completely satisfactory, as the table shows, and in this case, the time required for separation of beryllium from aluminum and iron under conditions where test material is given a preliminary treatment with a complexing agent is much shorter.

This method worked out for the determination of beryllium in the presence of aluminum and iron in synthetic mixtures by means of the cation exchange resin SBS was subsequently applied for the determination of beryllium in bronzes. In addition to the chief components (copper and beryllium) of the beryllium bronzes used, there was a number of other metals present, the chief of which were iron (up to 0.4%) and aluminum (up to 0.25%).

The following procedure was adopted for the analysis of bronzes: 0.5 g of the alloys was dissolved on heating in 25 ml of 30% nitric acid, and copper removed electrolytically in the solution obtained.

To this solution free of copper, ammonia was added until a faint odor was observed, when it was heated, and after 10 minutes filtered. The precipitate on the filter, which consisted of the hydroxides of beryllium, aluminum, and iron, was washed four times with a hot 2% solution of ammonium nitrate, and then dissolved in 20% hot hydrochloric acid. The filter was washed a few times with hot water. The solution was evaporated to a volume of 1 ml, after which it was cooled and diluted with 25 ml of water. To this solution was added 40 ml of 2% oxalic acid, 2 drops of methyl orange, and ammonia (dropwise) until the red color changed to yellow. This solution was passed through a column containing SBS in the hydrogen form at the rate of 2 ml/minute; beryllium was absorbed by the cation exchange resin while aluminum and iron passed into the filtrate. Traces of aluminum and iron were washed out of the column with water

at the rate of 4/5 ml/minute. Beryllium was completely removed from the column by eluting the column with 250 ml of hydrochloric acid. The filtrate containing the beryllium was treated with ammonia and then heated to 70°; after 10 minutes beryllium as hydroxide was filtered off through an ashless filter paper.

The precipitate was washed three times with hot 2% ammonium nitrate and after drying was calcined in a porcelain crucible at 1000° to give beryllium oxide.

The beryllium content was determined from the formula:

$$\% \text{ Be} = \frac{a \cdot 0.3605 \cdot 100}{m},$$

where a is the weight of beryllium oxide in g, 0.3605 is the conversion factor for beryllium oxide to beryllium, and m is the weight of sample taken, in g.

Results of beryllium determinations in bronzes by means of SBS are given in Table 3.

TABLE 3

Sample No.	Be found, in %					Be found, in % (gravimetrically with ammonia) after chromatographic separation.				
	CO	Gravimetric (orthohydroxy-quinoline method)								
110	2.12	2.23;	2.18;	2.22		2.07;	2.14;	2.08;	2.11;	2.10
452-1		2.18;	2.17;	2.20		2.08;	2.13;	2.08;	2.06;	2.07
452-2		2.19;	2.19;	2.23		2.14;	2.10;	2.12;	2.08.	
455-1		2.26;	2.28;	2.26		2.28;	2.23;	2.20;	2.20;	2.26
455-2		2.23;	2.20;	2.17		2.10;	2.14;	2.14;	2.10;	2.10
3		2.17;	2.15			2.05;	2.01;	2.02;	2.04;	2.08

Comparison of the results obtained for beryllium by the chromatographic method with results obtained by other methods shows that the chromatographic method gives satisfactory results.

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ORGANIC COPRECIPITANTS (COLLECTORS)

I. THE THEORETICAL BASES OF ORGANIC COPRECIPITANT ACTION

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A number of scientific and technical circles are at present showing increased interest in the presence of extremely small concentrations of individual elements in various materials. This is very important, particularly for geochemistry [1].

In order to carry out some of the analytical operations necessary for dealing with these traces, the methods of ordinary analytical chemistry are often inadequate [2]. In this connection, therefore, a new technique has had to be developed which is sometimes called the analytical chemistry of traces. One of the characteristics of this technique is preliminary concentration of the element, which is carried out by suitable ordinary methods.

For this preliminary concentration of elements coprecipitation of the elements is used, in which specially chosen so-called coprecipitants or collectors are used.

The action of many of the inorganic coprecipitants used is closely related to adsorption phenomena, the basic ideas for the use of which for coprecipitation of steel are well known from the work of V. I. Khlopin, K. Fajans, and O Khan, et al. The theoretical and practical side of the question has been treated in O. Khan's monograph [10].

Apart from the occasional use of organic ion exchange materials for element concentration, coprecipitants are almost invariably inorganic compounds, the applicability of which is not uniform in all cases.

The ideal coprecipitants are, of course, the isotopes of the coprecipitated elements [10]. The application of this type of coprecipitant (carrier) is confined to cases of precipitation of radioactive isotopes and to special cases of mass spectroscopic determination. Compounds of elements with properties very similar to the elements to be precipitated are sometimes good coprecipitants. An instance of this type is precipitation of one rare earth by another of the same group; radium with barium [10], astatine with tellurium [13], and certain others.

Compounds of low solubility and with a strongly developed surface [2, 15], are often used as inorganic precipitants, e.g., ferric hydroxide, alumina, hydrated manganese dioxide, sulfides [8, 11, 15], etc. Methods of using this type of collector are described in modern books on the determination of traces of elements [9].

In rare instances, e.g., as in the case of mercury compounds [17], the inorganic coprecipitant may be readily volatile. Such coprecipitants can be easily removed simply by heating the precipitates. In general the separation of the coprecipitated element from the inorganic carrier necessitates, as a rule, carrying out special additional operations, which do not always lead to the desired results. This complicates the use of inorganic coprecipitants when attempts are made to separate the coprecipitated element in the pure state free from carrier.

Other important disadvantages of inorganic precipitants are that their selectivity is not high enough; this is connected with the tendency of inorganic coprecipitants to adsorb various ions strongly, and the practical impossibility of controlling their selectivity.

In some cases organic precipitants can be found whose precipitating qualities can be forecast on the basis of the general theory of the action of organic reagents. The behavior of organic precipitants is readily controlled, and their selective coprecipitation properties are superior to those of inorganic precipitants. Organic precipitants, as indicated below, have little tendency to adsorb other ions, and the precipitates obtained are consequently purer than when inorganic coprecipitants are used. Organic coprecipitants can be removed from the required precipitates by simple combustion, thereby leaving the coprecipitated element in a pure state. This facilitates subsequent determination of the concentrated elements by any method.

Organic precipitants have already been in use for some time [12, 16] for carrying out preliminary concentration of elements for subsequent determination by spectrographic, X-ray spectrographic, and other methods. Organic coprecipitants carry this a stage further by lowering even more the limit to which the elements can be concentrated before determination.

The Impossibility of a Direct Application of the Coprecipitation Mechanism of Inorganic Coprecipitants to Organic Coprecipitants

Organic "Analogs" of Inorganic Ions

Organic compounds are known which give certain precipitation reactions analogous to the precipitation reactions of a number of inorganic ions. Thus benzidine precipitates sulfate ions in the same way as barium and strontium, while chloroplatinate ions are precipitated by many amines as well as by potassium, rubidium, cesium and some other elements.

The precipitation reactions of the cation diphenyliodonium $(C_6H_5)_2I^+$ is so similar to the precipitation reactions of Tl^+ that diphenyliodonium has been called "synthetic thallium," in the literature [20]. The solubility of diphenyliodonium salts is similar to the solubility of thallium salts; a mixture of the salts of these cations is not easily separated into its constituents by simple recrystallization, though it can be done chromatographically.

Such identical behavior in certain cases, however, is accidental. Organic "analogs" of inorganic ions show only an accidental or partial identity of behavior with corresponding inorganic ions in relation to the low solubility of certain of their salts in water. This identical behavior does not extend to the solubility of their other salts, or to solubility of these salts in other solvents apart from water.

Complete identity between organic anions and inorganic salts is impossible since the organic "analogs" differ appreciably from the corresponding inorganic ions in size, charge density, structure, number of electrons and their distribution, and in general in most other respects. E.g., the radius of the barium atom is 1.35 Å, while that of its organic "analog" benzidine is $\sim \pm 5$ Å [3].

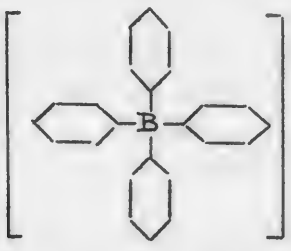
Salts of organic 'analogs' and salts of the respective inorganic ions do not form mixed crystals, are not isomorphous and are completely different crystallographically. This applies even to such closely related analogs as the diphenyliodonium cation and thallium [20]. As a result, difficultly soluble salts of organic analogs are not suitable coprecipitants for the respective inorganic ions. Attempts of the author to coprecipitate small amounts of strontium with the difficultly soluble benzidine sulfate did not give positive results.

Adsorption of Ions by Precipitates of Organic Compounds

Ionic adsorption on the surface of the precipitate formed is of great significance in coprecipitation with inorganic coprecipitants. The magnitude of this adsorption is closely related to the ionic character of the crystalline lattice of the precipitate and the presence of parts on the surface with strong fields.

Non-salt-like organic compounds crystallize in a molecular lattice. The crystal surface of these materials does not have areas with strong fields, so that the adsorption of ions on such crystals is manifest to only a very small degree. As a consequence of the large size of organic anions and cations, points with strong fields and a high charge density are absent even on crystals of salt-like organic compounds which, insofar as their capacity to adsorb ions is concerned, are inferior to inorganic materials.

There are direct indications in the literature of the incapacity of organic precipitates to adsorb ions. E.g., in a description of the removal of thionalide from solutions in the form of the disulfide, it is observed that in this case "the phenomenon of occlusion and adsorption is not manifest" [18]. An interesting example is the determination of potassium as $KB(C_6H_5)_4$. Here difficulties arise in connection with the volumetric variant of the determination. During volumetric determination of the boro-organic anion $B(C_6H_5)_4^-$ by titration with silver nitrate solution, which leads to the formation of a precipitate of $AgB(C_6H_5)_4$, the end point could not be determined when ordinary adsorption indicators were used, "...since the large $B(C_6H_5)_4^-$ anion adsorbs the silver salt only to an insignificant degree or not at all" [19].



These facts show up clearly the difficulty of trying to apply the known laws of inorganic adsorption to organic compounds, so that it would be unwise to search for organic coprecipitants, the action of which could be based only on adsorption phenomena. On the other hand, this weak tendency of organic precipitates to adsorb ions of elements is an advantage of organic coprecipitants, the action of which is based on other mechanisms, as this leads to the isolation of pure precipitates.

Coprecipitation with Organic Coprecipitants

Considered as Extraction with "Solid Solvents"

The experiments described below show that effective organic coprecipitants can be easily sought if coprecipitation is considered as extraction with "solid extracting agents."

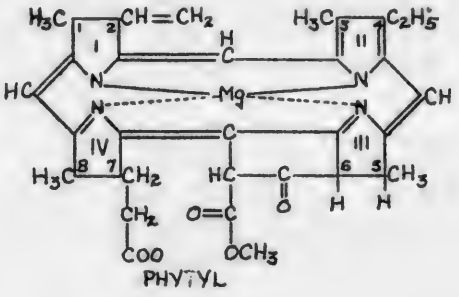
It is known that during precipitation of like materials, e.g., from an alcoholic solution by dilution with water, like materials precipitate simultaneously. The practice of purifying organic compounds shows that separation by similar methods, of mixtures of like materials, e.g., separation of members of a homologous series, is only carried out with great difficulty, the separation being more difficult the lower the solubility of the precipitated materials in dilute alcohol. By removal of one of the organic materials as a precipitate, it is possible to attract into the precipitate another similar organic compound of low solubility, traces of which were dissolved in the water or present in the water as a suspension.

In effect this process is completely analogous to extraction. It differs from ordinary extraction in that a solid material is used as the "extracting agent." If a suitable low melting product is used as a trapping agent, which on dilution of its alcoholic solution with water, separates out as a liquid, then the process will be a true extraction.

For successful coprecipitation, it is essential that there is the greatest possible similarity between the coprecipitated organic compound and the substance which is to be extracted as a precipitate. Numerous facts well known from the practice of purifying organic materials permit one to formulate the rule, "like precipitates like."

This rule which is completely analogous to the well known qualitative law defining the solubility of a substance, "like dissolves like," makes the search for organic coprecipitants of inorganic ions much easier.

Below we have adduced from P. Karrer's book [4], the formula of chlorophyll a, which contains magnesium.



One glance at this formula is enough to show that chlorophyll must be regarded as an organic material which has just these properties. Consequently, if when carrying out coprecipitation of magnesium it would be possible to convert magnesium into a compound similar to chlorophyll, coprecipitation of the compound obtained could be considered as coprecipitation of organic material.

As our experiments described below show, there is no need to convert the elements to be coprecipitated into such exceedingly complex compounds as chlorophyll in order to coprecipitate them. By successful choice of coprecipitant — excess of the precipitating organic reagent itself can sometimes be used — it is possible to effect coprecipitation by simply converting the element into a complex compound with such ordinary reagents as 8-hydroxyquinoline and similar precipitants.

In order to find out how far the action of organic coprecipitants of the category considered is comparable to extraction processes, two series of experiments were carried out in which the coprecipitant was the low melting product $C_6H_5 \cdot O \cdot C_6H_5$ (m.p. 27°). To a solution of cupric sulfate diluted to such an extent (5 μ g Cu in 250 ml) that 8-hydroxyquinoline does not give a direct precipitation of copper, was added with stirring an alcoholic solution of 2 mg of 8-hydroxyquinoline and 0.5 g diphenyl oxide. In one test the solution was heated up to 33° and the diphenyl oxide was in the form of an emulsion which, after cooling, set to a suspension. In the other test carried out at room temperature, a fine aqueous suspension of diphenyl oxide was first prepared, the copper solution was then added, followed by the 8-hydroxyquinoline. In both experiments the precipitates of diphenyl oxide were filtered, ashed, and copper determined in the residue. The amount of copper coprecipitated was the same in both cases, viz. 2.5 μ g.

These experiments and other similar ones show that in some cases at least, it is permissible to compare coprecipitation with extraction. This permits one to propose a priori that it is just as possible to extract elements from solution by coprecipitation as by extraction, from solutions just as dilute as can be handled by the latter. It should be remembered that extraction of the complexes of elements with organic precipitants can be more complete than direct precipitation with the same precipitants. This is well known from work on the complexes of 8-hydroxyquinoline [16], and others.

Coprecipitation with organic coprecipitants can also be compared with flotation reactions. This increases the number of compounds which can be dealt with, since in contrast to extraction in which all molecules must possess hydrophobic properties, for flotation reactions it is sufficient that only a part of the precipitated molecule should exhibit hydrophobic properties and have some properties in common with the precipitant.

Principles of Selecting Organic Precipitants

On the basis of the theoretical premises outlined above, which have also been checked experimentally, it is possible to select coprecipitants in practice by taking the following considerations for guidance.

1. When an organic reagent is used, the precipitated inorganic ion should be transformed into some compound in whose molecule the content of the organic part should be as high as possible.

2. It is desirable that the compounds of the element formed should be as insoluble as possible in the medium used.

3. Any organic compound which is of low solubility in the medium used and which has the closest structural similarity to the coprecipitated compound can be used as an organic coprecipitant of the compound of the inorganic ion obtained. It is convenient to introduce into the coprecipitant the same organic component which occurs in the coprecipitated compound of the test element.

4. In some cases the molecule of the organic coprecipitant may not have any great structural affinity with the molecule of the coprecipitated compound of the inorganic ion ("indifferent" coprecipitants, see below).

Coprecipitation of Normal Salts Containing an Organic Part with a High Molecular Weight

If the coprecipitated element is capable of forming complex anions, about which it is also possible to judge from the capacity of the element to give so-called colored solid phase reactions [7], then salts of organic cations which are practically insoluble, have a high ionic weight, and contain those

same addenda that were used for forming the complex anion of the element should be very suitable coprecipitants.

E.g., on the basis of colored solid phase reactions [5] and other facts, it is known that zinc forms a characteristic weakly dissociated anion $Zn(SCN)_4^{2-}$, in which form, using methyl violet and other basic dyes, zinc can be precipitated from fairly weak solutions. Zinc can, however, be coprecipitated from even more dilute solutions in conjunction with a precipitate of the relatively insoluble thiocyanate cation of methyl violet. On the basis of experiments carried out by the author together with E. S. Pashin and E. V. Mitrofanova, it was found convenient to carry out the test as follows: To a weakly acid solution containing traces of zinc was added a small amount of ammonium thiocyanate; this was followed by methyl violet, and after this some more ammonium thiocyanate sufficient for precipitation of the methyl violet cations as thiocyanate. The precipitate was filtered, washed, ashed, and the coprecipitated zinc determined in the residue. From a volume of 100 ml, 1 μg of zinc was coprecipitated completely.

In addition to zinc, other elements which form complex thiocyanate anions – Bi, Cu, and Cd and many others[1)] can be coprecipitated in exactly the same way as zinc with methyl violet thiocyanate.

It is convenient to coprecipitate elements forming complex iodide anions with the iodides of methyl violet, methyl blue, aminoazo compounds, and other basic dyes.

It is possible by similar means to coprecipitate the most varied complex anions and cations of elements. Cations can be coprecipitated as the salts of high molecular weight aliphatic or other acids, using these acids or their salts with organic bases as the coprecipitant.

If the basic dye used does not form a sufficiently insoluble salt with the anions used as addenda, then this basic dye can be precipitated by some other organic anion with a greater ionic weight. E.g., the ammonium salts of anthraquinone sulfonic acid and of the monosulfonic acids of azo-compounds, and many other compounds, are suitable.

Another example is the coprecipitation of phosphorus, which in the experiments of the author and E. S. Palshin was completely coprecipitated from 10^{-10}-10^{-11} M solutions of phosphates. Ammonium molybdate was added to the acidified solution of phosphate, and the mixture heated to form the phosphomolybdate heteropoly acid; methyl violet was then added, and in order to precipitate this, ammonium anthraquinone-α-sulfonate was added. The precipitate which separated out was filtered off, washed, and ashed.

Coprecipitation of Complex and Inner Complex Salts of the Elements. "Indifferent Coprecipitants."

The organic coprecipitants considered above may be regarded simply as excess of an organic precipitant of low solubility or of the practically insoluble salt of such a precipitant. The drawback of coprecipitants of this type is that their selectivity is not high enough. The highest selective coprecipitation is shown by indifferent coprecipitants by which we mean coprecipitants which do not contain components which cause direct precipitation of the elements. Indifferent coprecipitants fit very well into the class of

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1) A method described recently for purifying salts was based on this principle; salts of Ni, Mg, and Cr are purified from Zn, Cd, Hg, Bi, Co and Cu, the latter being completely precipitated after addition of thiocyanates and diantipyrylmethane hydrochloride [21].

"solid extracting agents." Coprecipitants of this type may be of a different kind altogether from the coprecipitated compound. Of particular interest are coprecipitants which do not contain salt-forming or complexing groups, since such coprecipitants show very little tendency to adsorption of ions from solution, and therefore give particularly pure precipitates.

The esters of the corresponding organic precipitates should from general considerations be particularly suitable as indifferent coprecipitants for the precipitation of inner complex salts of the elements. E.g., the dialkyl ester of dimethylglyoxime should be a suitable coprecipitant for the coprecipitation of nickel dimethylglyoxime. The esters of the precipitants are more suitable as coprecipitants than the organic precipitants themselves, since the inner complex compounds of the elements are more like the esters of the organic precipitants than the precipitant itself. The use of excess of an organic precipitant as a coprecipitant is less convenient, and a consequence of its use will be a less pure precipitate, as observed, e.g. in cupferron precipitates [14].

Apart from the coprecipitation of inner complex compounds, indifferent coprecipitants are equally suitable for the coprecipitation of compounds which are normal salts, e.g. for the precipitation of the salt of the methyl violet cation with the complex thiocyanate anion of zinc $Zn(SCN)_4^{2-}$.

The use of indifferent coprecipitants is particularly attractive because they do not require the introduction of large amounts of some other reagent to the solutions, e.g. addition of NH_4SCN as in coprecipitation with precipitates of methyl violet thiocyanate. Consequently when indifferent coprecipitants are used, current analytical methods in which selectivity has been thoroughly studied may be applied. E.g., zinc was precipitated successfully at a dilution of $1:10^7$ and in even more dilute solutions on using phenolphthalein as a coprecipitant and working directly under the conditions recommended for carrying out the highly selective colored solid-phase reaction for zinc with thiocyanates and methyl violet [5].

It is convenient to use indifferent coprecipitants in the form of their alcoholic or acetone solutions. On pouring these solutions into water, the dissolved coprecipitant separates out as a precipitate and traps the compound to be coprecipitated. There are as yet no general theoretical considerations which can be used as a basis of a search for the most suitable coprecipitant in each individual case. One must look for these coprecipitants experimentally, and this should not prove too difficult. E. V. Mitrofanova, while carrying out experiments on the precipitation of organic dyes of various classes from aqueous solutions, found that phenolphthalein, α-naphthol, m-nitrobenzoic acid, and β-hydroxynaphthoic acid are good coprecipitants.

Improving the Completeness of the Precipitation of Elements with Organic Precipitants.

The use of organic precipitants permits one to extend the limits of application of organic precipitation to solutions of lower concentrations of the elements to be precipitated. Such an extension of the limits can be realized by combining organic precipitants with extraction, as noted in the literature [10]. When organic precipitants are used, this is conveniently achieved.

In noting the great practical importance of the possibility of improving the completeness of precipitation of the elements by using organic precipitants, we shall confine ourselves to only one example. At a dilution of $1:10^7$, nickel is not precipitated by 8-hydroxyquinoline. Even when a large amount of macerated paper is used, no nickel is present in the paper mass filtered off. When however β-naphthol is used as a coprecipitant under the same conditions, complete precipitation of nickel is observed even at dilutions of $1:5\cdot10^8$ (E. V. Mitrofanova).

The Selective Action of Organic Coprecipitants

The selective action of coprecipitants which are salts of low solubility is fully understood.

All those elements which have ions identical in structure and properties with the coprecipitated ions of the elements being coprecipitated can be coprecipitated with this type of coprecipitant. E.g., on coprecipitating zinc in the form of the methyl violet salt with the anion $Zn(SCN)_4^{2-}$, all the other elements which form complex thiocyanate anions precipitated with methyl violet, i.e. Cd, Cu, and Hg, etc., will be trapped into the precipitate at the same time as the precipitate of methyl violet thiocyanate. In addition, all those other elements will be coprecipitated which are present in solution, generally in the form of large, hydrophobic anions which form salts of low solubility with such large cations as the methyl violet cation. Examples of such anions are the tungstates[1], heteropoly acids, and various complex anions such as $AuCl_4^-$, $SbCl_6^-$, et al. Coprecipitations of this type are completely understood and are easy to foresee.

The fact that the underlying mechanism of coprecipitation is clear in individual cases permits coprecipitation to be controlled. In order to prevent coprecipitation of individual elements, it is necessary to convert them into hydrophilic complexes by addition of tartrates, citrates, and similar hydrophilic masking complexing agents. If these complexing agents do not convert the element to be coprecipitated into hydrophilic ions as well, then the selectivity of coprecipitation can be increased. In general, the selective action of organic precipitants which are salts is low, the more so because the introduction of large amounts of the precipitating ions, e.g. thiocyanate ions during precipitation of methyl violet thiocyanate, favors conversion into precipitated complex ions even of elements which show little tendency to do so.

The selective action of indifferent coprecipitants is higher. Of particular value is the fact that these coprecipitants, as noted already, can be used directly in the reaction media which are recommended in current methods for the precipitation of elements and for colorimetric determinations on the basis of colored solid phase reactions. Coprecipitation selectivity is almost the same as the selectivity of the respective reactions. A displacement of equilibrium can only occur as a result of a particularly complete separation of an element from a system by coprecipitation.

Questions of increasing the selectivity of analytical reagents are the most difficult questions of contemporary analytical chemistry. At present the most real and positive method of solving this question of selectivity is to develop for each element "two different precipitants" which, apart from precipitation phenomena is of general interest for the analytical chemistry of a given element.

By this term "the two precipitant method" we mean the presence of two precipitants of a given element, in our case of two coprecipitants, which would precipitate a given element on the basis of reactions with two completely different mechanisms. E.g., one precipitant would precipitate the element as a cation, while the other precipitant would precipitate it in the form of some complex anion. During the first precipitation, other elements will be precipitated in addition to the element in which we are interested, but probably not all those originally present in solution; some of

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1) Coprecipitation of tungsten is incomplete in this case. Complete coprecipitation of tungsten at dilutions of $1:10^9$ and more is achieved by simultaneous addition of tannin (experiments of the author and E. S. Palshin).

the elements will have been removed. After filtration, the organic reagent contained in the precipitate will be destroyed by ignition, the residue dissolved, and a new precipitation carried out using the second precipitant, which is selected so that not one of the other elements which may be present in the first precipitate will be trapped in the precipitate of the second precipitation.

As an example of the application of this method in which two selected organic reagents are used, we shall quote the published method [6] of determining tin in complex mixtures. In this case, tin (Sn IV, β-compounds) is initially coprecipitated from an acid solution with anthraquinone-α-arsonic acid, Zr, Hf, Nb, Ta, and Ti being coprecipitated simultaneously. After destruction of the reagent left in the precipitate and dissolving the tin, the latter is colorimetrically determined with the reagent "antrazo" (anthraquinone-<1-azo-4>-dimethyl aniline) on the basis of a colored solid phase reaction in which the capacity of tin to form anions of the form $Me^{IV}Cl_6^{2-}$ x x ($SnCl_6^{2-}$) is used.

A technique similar to that of "the two-precipitant method" was used by V. T. Chuiko for coprecipitation of nickel in order to separate it from elements of the fourth analytical group [11].

Good results are also obtained when one precipitant is used and the two valency states of the element are made use of; in this case the element is precipitated when in one of these valency states and not in the other. According to the author's and G. Grinevich's work, trivalent (but not univalent) thallium is quantitatively precipitated even at dilutions of $1:10^{10}$ from 0.2 N HCl with the precipitate formed between p-dimethylaminobenzene and methyl orange. The procedure adopted, therefore, is first to keep the thallium in the univalent state and precipitate all those elements which can be precipitated by the precipitant used, then after oxidizing the Tl^{I} to Tl^{III} ($TlCl_4^-$) by addition of the same reagent, the thallium can be coprecipitated and separated from the other elements.

SUMMARY

Organic coprecipitants are of great interest for preliminary concentration of micro amounts of elements before determining them quantitatively by the usual methods. The advantage of organic coprecipitants as compared to inorganic coprecipitants are: ease of removal of organic coprecipitants from precipitates by simple ignition, the practical absence of adsorption of other ions by many organic precipitants, the ease with which coprecipitation can be controlled, their well-known selective action.

Coprecipitated elements must be converted into compounds of low solubility, which contain as much as possible of the organic component. The compound of the element obtained should, if possible, be similar to the practically insoluble organic compound acting as coprecipitant. Inner complex, complex, and also normal salts of the elements containing a large organic part are suitable for coprecipitation. E.g., the difficultly soluble salts of the cations of methyl violet or methylene blue with the complex anions of the elements are suitable. Practically insoluble salts of the same organic cations with heavy, volatile, inorganic or organic anions can be used as coprecipitants.

Non-salt-like organic compounds ("indifferent" coprecipitants) can also be used as coprecipitants; their action can be considered as "extraction with solid solvents." The use of "indifferent" coprecipitants permits the concentration limit at which elements can be removed by organic precipitants to be extended.

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[2)] See Consultants Bureau Translation, page 1.

QUALITATIVE ANALYSIS OF SILICO-ORGANIC COMPOUNDS BY INFRARED ABSORPTION SPECTROSCOPY

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Chemical methods of analyzing silico-organic compounds which are based on the capacity of the test material to give some characteristic reaction, do not always permit the exact determination of the composition of the test product. On the other hand, physical and physico-chemical methods of analysis such as spectral molecular analysis in the infrared, permit the problem to be solved relatively easily to give reliable results.

Comparative test methods are usually used when dealing with the spectra of complex molecules. For this purpose the absorption spectra of a number of structurally similar compounds have been studied, e.g., of a homologous series, since this brings out the similarities and differences in the absorption spectra. Using this method it is possible to establish a number of principles and apply infrared spectroscopy to structural problems. E.g., the presence of $-CH_3$ and $=CH_2-$ in a molecule leads to absorption near 3 μ. A large amount of work which has been carried out along these lines has enabled us to establish that the respective absorption bands are determined by the vibrations of definite atomic groupings or bonds and are practically independent of the rest of the molecule [1,2]. Vibrations corresponding to characteristic frequencies are concentrated in one bond of the molecule (a definite atomic grouping), while the remaining atoms have no essential effect on them. That is why, e.g., the frequency of the C–H bond is maintained a constant in all the homologs, irrespective of the position of the molecule in a homologous series. By a study of these characteristic frequencies, it is possible to sort out the absorption spectra of complex molecules and to assign each characteristic band to its respective frequency and to clarify a number of structural characteristics of the molecules. The position of characteristic frequencies in a spectra can be displaced considerably under the influence of a number of factors, such as the mass of the neighboring atoms, the nature of the bond, etc. This shift can also occur when not only the atoms of a given bond vibrate but the rest of the molecule as well. E.g., the characteristic absorption band of the C–H bond can be shifted to either the short or long wave length side of the spectra according to the structure of the molecule.

By gathering all the experimental data available, tables have been compiled (Tables 1 and 2) [3], for the characteristic vibration frequencies of groups of atoms and of the most important bonds.

The infrared spectra of homologs and isomers as shown experimentally have much in common. Nevertheless, they are clearly distinguishable from each other since each individual substance has its own non-recurring spectrum. On the basis of the application of infrared absorption spectra, the following problems can be solved: the identification of a substance by means of its infrared spectrum, proving the presence of definite atomic groupings

and chemical bonds in a molecule, identification of mixture components, establishment of the presence of tautomeric forms, and determining small amounts of contaminants present in test mixtures, etc.

The infrared absorption spectra of silico-organic compounds have not hitherto been studied to any significant extent. Published data [4-7] is insufficient to establish with a reasonable degree of accuracy what absorption bands are determined by which specific atomic groupings, and to establish the characteristics of certain bonds.

In this paper the infrared absorption spectra of the most important silico-organic compounds have been studied.

TABLE 1

Characteristic Vibration Frequencies of Atomic Groups and of the Most Important Bonds in Organic Compounds

Group	Fundamental		Overtones									
	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}
$=CH_2$ and $-CH_3$	3.39 3.48	2950 2870	1.74	5740	1.19	8400	0.909	11000	0.630	15860	0.549	18214
$=CD_2$ and $-CD_3$	4.54	2200	–	–	–	–	–	–	–	–	–	–
–OH (free)	2.75	3630	1.40	7100	0.961	10400	0.740	13500	–	–	–	–
–OH (bound)	2.98	3350	1.60	6250	1.04	9605	–	–	–	–	–	–
–OD (free)	3.29	3040	–	–	–	–	–	–	–	–	–	–
–OD (bound)	3.76	2660	–	–	–	–	–	–	–	–	–	–
=NH and $-NH_2$	3.03	3300	1.53	6530	1.04	9650	0.806	12400	0.666	15000	–	–
–SH	3.84	2600	2.00	5000	–	–	–	–	–	–	–	–
=C=C=	6.06	1650	–	–	–	–	–	–	–	–	–	–
–C≡C–	4.50	2220	–	–	–	–	–	–	–	–	–	–
$-NO_2$	7.24	1380	–	–	–	–	–	–	–	–	–	–
–N=C=S	4.55	2150	–	–	–	–	–	–	–	–	–	–
–C≡N	4.44	2250	–	–	–	–	–	–	–	–	–	–
=C=O	5.81	1720	2.90	3440	1.90	5260	1.45	6890	1.16	8600	0.970	10309

TABLE 2

Characteristic Vibration Frequencies of Atomic Groups and of the Most Important Bonds in Inorganic Compounds

Group	Fundamental		Overtones					
	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}
$-NO_2$ (nitrite)	12.25	820	8.25	1220	7.65	1320	–	–
$-CO_3$ (carbonate)	14.25	700	11.50	870	9.50	1060	6.66	1500
$-NO_3$ (nitrate)	15.50	650	12.25	820	–	–	7.14	1400
$-ClO_3$ (chlorate)	23.00	434	16.00	624	10.50	950	10.06	994
$-BrO_3$ (bromate)	29.07	344	23.00	434	12.50	800	12.25	820
$-IO_3$ (iodate)	31.05	322	28.01	357	12.75	780	10.06	793

EXPERIMENTAL

The objects of our tests were certain compounds of the following types: alkoxy-, aroxysilanes, alkyl and arylalkoxysilanes, alkyl and arylsilanes, and siloxanes.

The basic materials were synthesized by published methods [8]. The synthesized compounds were carefully purified by chemical and physical methods.

Final separation of the chemically pure compounds was effected by means of a rectifying column.

Physical constants for the products obtained are given in Table 3.

TABLE 3

Physical Constants of the Silico-Organic Compounds Synthesized

Formula and Designation of Compound	B.p. and m.p. in °C	D_4^{20}	n_D^{20}
Tetramethoxysilane $(CH_3O)_4Si$	121.4	1.0390	1.3681
Tetraethoxysilane $(C_2H_5O)_4Si$	166	0.9345	1.3830
Tetrabutoxysilane $(n\text{-}C_4H_9O)_4Si$	151.5 (16 mm)	0.9528	1.4132
Tetraisoamyloxysilane $(i\text{-}C_5H_{11}O)_4Si$	175 (12 mm)	0.8760	1.4180
Tetraphenoxysilane $(C_6H_5O)_4Si$	418; 52	–	–
Tetramethylsilane $(CH_3)_4Si$	26.8 (756 mm)	0.6466	1.3590
Tetraphenylsilane $(C_6H_5)_4Si$	530; 233	1.078	–
Trimethylallylsilane $(CH_3)_3SiCH_2CH{=}CH_2$	85.4 (760 mm)	0.7195	1.4075
Dimethyldiethoxysilane $(CH_3)_2Si(OC_2H_5)_2$	114 (742 mm)	0.8395	1.3810
Trimethylethoxysilane $(CH_3)_3Si(OC_2H_5)$	75 (745 mm)	0.7573	1.3742
Hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$	100 (742 mm)	0.7638	1.3773

The infrared absorption spectra of the silico-organic compounds were studied on a Hilger spectrometer. The infrared ray receiver was a thermocolumn with a silver-cadmium thermocouple; the source was a Silit resistor 96 mm long and 8 mm in diameter which was heated with a current of 16 A at 48 V.

In order to maintain the radiation from the Silit resistor constant, the current used was stabilized with a precision stabilizer.[1)]

1) The stabilizer was constructed specially for this work by V. D. Matveev, an assistant in the Institute.

Since silico-organic compounds absorb the infrared strongly, the absorption spectra were photographed in carbon tetrachloride solution. The carbon tetrachloride was specially purified.

Tetraphenylsilane was examined as a powder. Measurements were made in the 2-10 μ region. The transmission curves of the compounds studied are given in Figs. 1-12.

DISCUSSION OF RESULTS

As the transmission curves show, one of the characteristic features of the infrared absorption spectra of the silico-organic compounds is the presence of strong absorption bands at 7-10 μ (1429-1000 cm^{-1}). A band is observed at 7.9-8.0 μ (1266-1250 cm^{-1}) in the infrared spectra of all compounds in which there are methyl groups connected to silicon. According to published results an absorption band is observed at 7.25 μ (1379 cm^{-1}) in the absorption spectra of aliphatic hydrocarbons $R - CH_3$, which is determined by the deformation vibration of the $C\begin{matrix}H\\ \diagup\\ -H\\ \diagdown\\ H\end{matrix}$ bonds in the CH_3 groups. The presence of a band at 7.9-8.0 μ (1266-1250 cm^{-1}) is therefore apparently the result of the vibration of the Si – C bond in the group $\equiv Si - CH_3$. This hypothesis is confirmed by the fact that in the spectra of silico-organic compounds where there is no $\equiv Si - CH_3$ group, e.g., in the spectra of alkoxy and aroxysilanes (esters of orthosilicic acid) with the general formula $Si(OR)_4$, the band with maximum absorption at 7.9-8.0 is absent.

A band is observed at 9.5-9.6 μ (1053-1042 cm^{-1}) in the infrared absorption spectrum of all the silico-organic compounds in which silicon is linked with oxygen.

A band with wave number 1111 cm^{-1} [9] is observed in carbon compounds which contain an ester link. This frequency is interpreted as a characteristic frequency of the C – O bond. It can be assumed therefore that the band at 9.5-9.6 μ (1053-1042 cm^{-1}) is determined by the longitudinal vibration of the Si – O bond.

Yet another band is observed at 8.6-8.7 μ (1163-1149 cm^{-1}) in the infrared spectrum of alkoxy-and aroxysilanes with the general formula $Si(OR)_4$, and in the spectrum of alkyl- and arylalkoxysilanes. The wave number of this band is characteristic of the frequency of the bond O – R of the ester group [9]. This band is shifted in the spectra of tetraphenoxysilane $(C_6H_5O)_4Si$ to 8.05 μ (1242 cm^{-1}).

Apart from the absorption band which is caused by vibration of Si – C and Si – O bonds which are specific for silico-organic compounds, other characteristic absorption bands of certain atomic groups or bonds can be observed in the infrared absorption spectra of these compounds.

In compounds containing the methyl groups linked with an aliphatic radical, bands are observed at 3.47 μ (2879 cm^{-1}), 6.9 μ (1449 cm^{-1}) and 7.24 μ (1380 cm^{-1}) [2]. The vibration frequency of the first band is a characteristic frequency of valency vibrations of the $C\begin{matrix}H\\ \diagup\\ -H\\ \diagdown\\ H\end{matrix}$ bond, while the vibration frequencies of the other bands are characteristic frequencies of the deformation vibrations of this bond.

According to published results [10], bands, the vibration frequencies of which are characteristic for the bonds $C\begin{matrix}H\\ \diagup\\ \\ \diagdown\\ H\end{matrix}$ and C – H in the groups $=CH_2$ and $\equiv CH$ in aliphatic compounds $R'R''CH_2$ and $R'R''R'''CH$, are very near

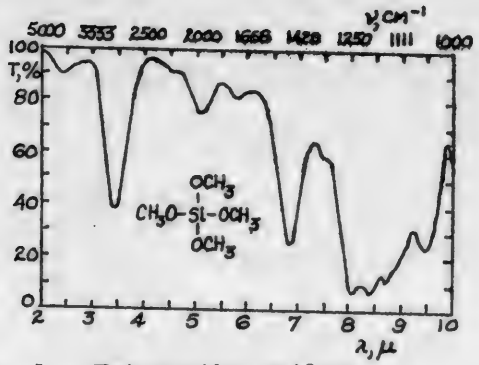

Fig. 1. Tetramethoxysilane. 3.45(2899)38; 6.85(1459)25.4; 8.05 (1242)7, 8.4(1190)7; 8.7(1149)11.5; 9.5(1053)24.

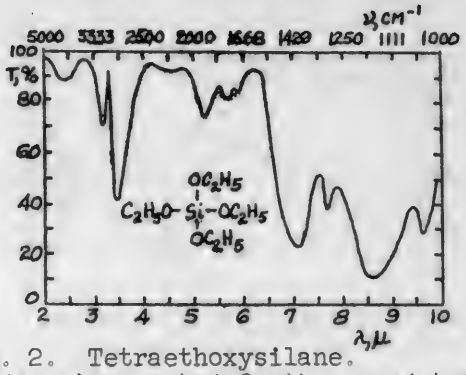

Fig. 2. Tetraethoxysilane. 3.2(3125)70; 3.45(2899)41; 7.1(1408) 23, 7.7(1299)37.4; 8.6(1163)10, 9.6(1042)28.

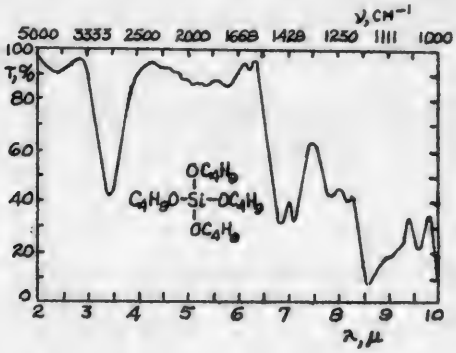

Fig. 3. Tetrabutoxysilane. 3.45(2899)42; 6.85(1459)31.2; 7.1 (1408)32.2; 7.85(1274)42.2; 8.2(1220) 41; 8.6(1163)8, 9.6(1042)21.

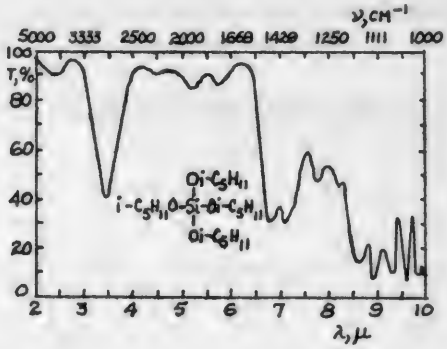

Fig. 4. Tetraisoamyloxysilane. 3.45(2899)40.4; 6.8(1471)31; 7.1 (1408)30; 7.75(1290)47; 8.2(1220) 45.5; 8.6(1163)14.5; 8.9(1124)8; 9.3(1075)10.5; 9.6(1042)7; 9.8(1020) 10.

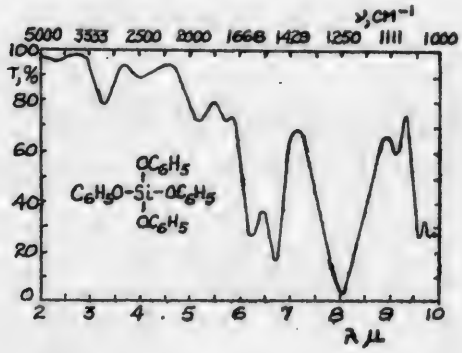

Fig. 5. Tetraphenoxysilane. 3.25(3077)78; 6.25(1600)27; 6.7(1493) 18; 8.05(1242)3; 9.1(1099)60; 9.6 (1042)26; 9.8(1020)26.4

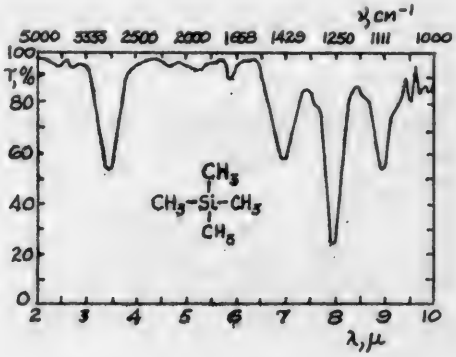

Fig. 6. Tetramethylsilane. 3.45(2899)54; 6.95(1439)57.4; 7.95 (1258)24; 8.95(1117)54; 9.5(1053) 80; 9.7(1031)83.4; 9.9(1010)85.

Figs. 1-12 represent the infrared absorption spectra of silico-organic compounds and of 25% solutions of the same compounds in carbon tetrachloride. The first number denotes the wave length in microns, while the second (in parenthesis) denotes the wave numbers characteristic of the vibration in cm^{-1}, and the third number the transmission in %.

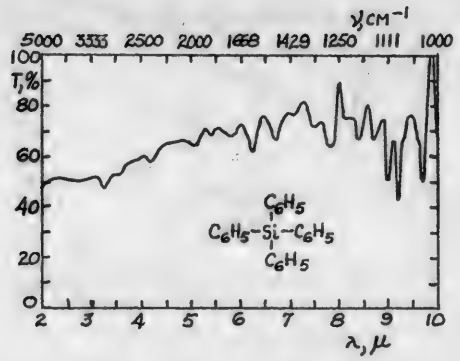

Fig. 7. Tetraphenylsilane.
3.25(3077)47; 6.25(1600)62; 6.7(1493) 66; 7.5(1333)71.4; 7.8(1282)64; 8.4 (1190)66.6; 8.7(1149)67; 9.0(1111)50; 9.2(1087)43, 9.7(1031)50.

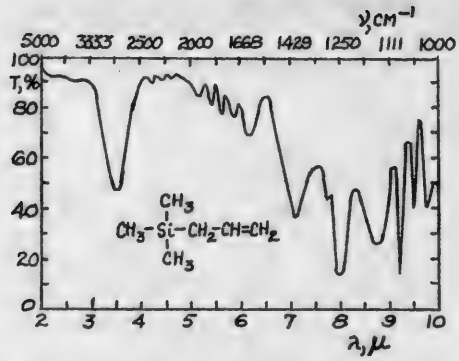

Fig. 8. Trimethylallylsilane.
3.5(2857)47; 6.15(1626)69; 7.1(1408) 36; 7.7(1299)44.4; 8.0(1250)13.6; 8.75(1143)26; 9.2(1087)13; 9.5(1053) 40; 9.75(1026)40.

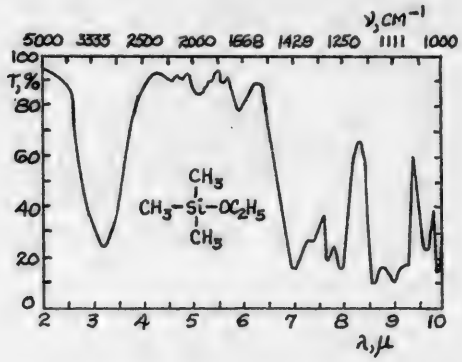

Fig. 9. Trimethylethoxysilane.
3.2(3125)24; 7.0(1429)15.4; 7.7(1299) 19; 7.95(1258)15; 8.6(1163)10; 9.0 (1111)10; 9.65(1036)23.5; 9.9(1010)14.

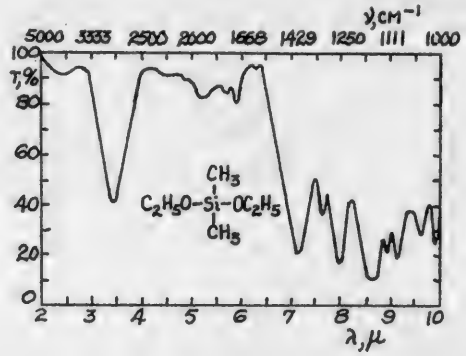

Fig. 10. Dimethyldiethoxysilane.
3.45(2899)41; 7.1(1408)20.4; 7.6 (1316)6; 7.95(1258)15.2; 8.6(1163) 10; 8.9(1124)21; 9.1(1099)18; 9.6 (1042)28; 9.9(1010)25.

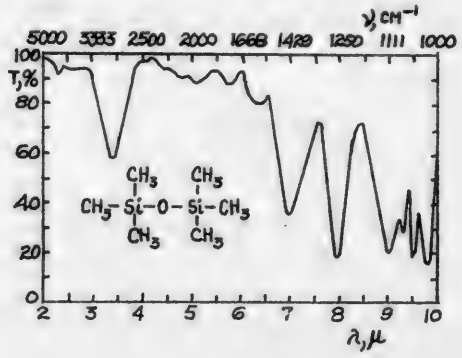

Fig. 11. Hexamethyldisiloxane.
3.4(2941)57.7; 6.95(1439)35; 7.95 (1258)18.2; 9.0(1111)20; 9.3(1075) 28, 9.5(1053)19, 9.8(1020)16.

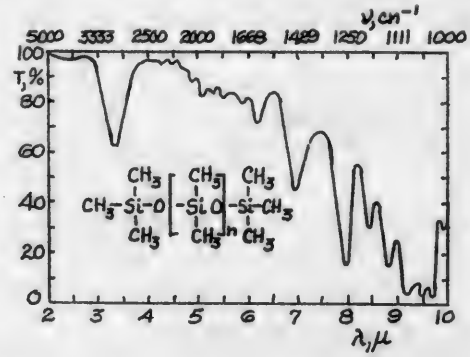

Fig. 12. Silicone oil.
3.35(2985)62, 6.2(1613)71; 6.95 (14 9)45.4; 7.95(1258)16; 8.4(1190) 30; 8.8(1136)14.4; 9.2(1087)3.5; 9.5(1053)3.0; 9.7(1031)2.4; 9.9(1010) 30.

to each other. The dispersion of the rock salt (from which the spectrophotometer prism is made) in the spectral region 3-4 μ does not permit identification of absorption bands characteristic of the groups $=CH_2$ and $\equiv CH$. In silico-organic compounds containing the phenyl groups such as $(C_6H_5)_4Si$, bands are observed at the following wave lengths 3.25 μ (3077 cm^{-1}), 6.25 μ (1600 cm^{-1}), 6.7μ (1493 cm^{-1}) and 9.7 μ (1031 cm^{-1}).

According to published results [2], absorption bands are observed in this region in the absorption spectra of unisubstituted benzene compounds of the type C_6H_5X. The bands observed are therefore probably caused by the presence of phenyl groups.

A band is observed at 6.15 μ (1626 cm^{-1}) in the infrared absorption spectra of trimethylallylsilane $(CH_3)_3Si-CH_2-CH=CH_2$ which is determined by the groups $-CH=CH_2$. This is confirmed by the fact that an absorption band is observed just in this very region in the infrared absorption spectra of molecules containing the $-CH=CH_2$ group [2].

A summary of the results obtained is given in Table 4.

1. A methyl group is present in the test material when bands with maximum absorption are observed at 3.35-3.5 μ (2985-2857 cm^{-1}) and at 6.8-7.1 μ (1471-1408 cm^{-1}).

2. The silicon atom is directly linked to a methyl group when bands are present at 7.95-8.0 μ (1258-1250 cm^{-1}).

3. A phenyl group is present when bands are observed at 3.25 μ (3077 cm^{-1}), 6.25 μ (1600 cm^{-1}), 6.7 μ (1493 cm^{-1}) and 9.7 μ (1031 cm^{-1}).

4. A Si-O group is present in the test compound if bands are observed at 9.5-9.65 μ (1053-1036 cm^{-1}) while an ester group is present $\equiv Si-O-R$ if bands are observed at 8.6-8.7 μ (1163-1149 cm^{-1}).

5. A $-CH=CH_2$ group is present if a band is observed at 6.15 μ (1626 cm^{-1}).

These facts permit one to establish the presence of a number of atomic groupings in an unknown silico-organic compound. On the basis of these results it is possible to establish to a certain extent to what class the given silico-organic compound belongs.

1. Alkyl- and Arylsilanes. Alkylsilanes which contain the atomic group $\equiv Si-CH_3$ are characterized by the fact that a band is observed at 7.95-8.0 μ (1258-1250 cm^{-1}), which is determined by the Si-C bond in the group $\equiv Si-CH_3$. In addition, the spectra of these compounds contain bands at 3.35-3.5 μ (2985-2857 cm^{-1}) and at 6.8-7.1 μ (1471-1408 cm^{-1}), which are characteristic of the $-CH_3$ group. Bands resulting from the presence of the Si-O bond are absent. The use of a spectrographic apparatus with a large dispersion makes the establishment of the presence of the atomic group $-CH_3$, $=CH_2$ and $\equiv CH$ possible.

Arylsilanes are characterized by the fact that bands are present in the spectra of these compounds at 3.25 μ (3077 cm^{-1}), 6.25 μ (1600 cm^{-1}), 6.7 μ (1493 cm^{-1}) and 9.7 μ (1031 cm^{-1}), which are characteristic for the C-H bonds in the benzene ring.

2. Alkoxy- and Aroxysilanes (esters of orthosilicic acid), are characterized by the presence of a band at 9.5-9.65 μ (1053-1036 cm^{-1}), in the spectra of these compounds which is determined by the Si-O bond and a band at 8.6-8.7 μ (1163-1149 cm^{-1}), which is determined by the ester group $-O-R$.

3. Alkyl- and Arylalkoxysilanes are characterized by the presence of a band at 9.5-9.65 μ (1053-1036 cm^{-1}) in the spectra and at 8.6-8.7 μ (1163-1149 cm^{-1}), which are determined by the Si-O bond and the ester group $-O-R$.

TABLE 4

Wave Numbers of the Characteristic Vibrations of Atomic Groupings and of the Most Important Bonds of the Silico-Organic Compounds Examined (Wave lengths in microns, wave numbers in cm^{-1})

Formula and designation of compound	$-CH_3$; $C\begin{smallmatrix}H\\-H\\H\end{smallmatrix}$		C_6H_5-; C–H	
	μ	cm^{-1}	μ	cm^{-1}
Tetramethoxysilane $(CH_3O)_4Si$	3.45	2899	–	–
Tetraethoxysilane $(C_2H_5O)_4Si$	3.45	2899	–	–
Tetrabutoxysilane $(n\text{-}C_4H_9O)_4Si$	3.45	2899	–	–
Tetraisoamyloxysilane $(i\text{-}C_5H_{11}O)_4Si$	3.45	2899	–	–
Tetraphenoxysilane $(C_6H_5O)_4Si$	–	–	3.25 6.25 6.7 9.7	3077 1600 1493 1031
Tetramethylsilane $(CH_3)_4Si$	3.45	2899	–	–
Tetraphenylsilane $(C_6H_5)_4Si$	–	–	3.25 6.25 6.7 9.7	3077 1600 1493 1031
Trimethylallylsilane $(CH_3)_3SiCH_2-CH=CH_2$	3.5	2857	–	–
Trimethylethoxysilane $(CH_3)_3Si(OC_2H_5)$	3.2	3125	–	–
Dimethylethoxysilane $(CH_3)_2Si(OC_2H_5)_2$	3.45	2899	–	–
Hexamethyldisiloxane $(CH_3)_3SiOSi(CH_3)_3$	3.40	2941	–	–

If these compounds contained the methyl group, bands which are determined by the Si–C bond in the group $\equiv Si-CH_3$ and by the $C\begin{smallmatrix}H\\-H\\H\end{smallmatrix}$ bond in the $-CH_3$ group should be observed.

4. Siloxanes are characterized by the appearance in their spectra of a band at 9.5 9.65 μ (1053-1036 cm^{-1}), which is determined by the Si–O bond, while the band at 8.6 8.7 μ (1163-1149 cm^{-1}), which is determined by the ester group, is absent.

The final stage in our work was the testing of a technical product, "Silicone Oil."

In the infrared absorption spectra of "Silicone Oil" the following bands were found to be present: ones with maximum absorption at 3.4 and 6.95 μ which are determined by the characteristic vibration of the methyl group, one with maximum absorption at 7.95 μ, determined by the presence of a methyl group on a silicon atom, and a band with maximum absorption at 9.5 μ which is determined by the bond between silicon and oxygen.

On the basis of the results obtained, it may be considered that the test organo-silicon compound contains the atomic groups and bonds listed above.

TABLE 4 (continued)

$-CH_3$; $C\begin{smallmatrix}H\\H\\H\end{smallmatrix}$		$\equiv Si-CH_3$; Si–C		Si–O		$-CH_2-CH=CH_2$; C=C		–O–R	
μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}	μ	cm^{-1}
6.85	1459	–	–	9.5	1053	–	–	8.7	1149
7.1	1408	–	–	9.6	1042	–	–	8.6	1163
6.85 7.1	1459 1408	–	–	9.6	1042	–	–	8.6	1163
6.8 7.1	1471 1408	–	–	9.6	1042	–	–	8.6	1163
–	–	–	–	9.6	1042	–	–	8.05	1242
6.95	1439	7.95	1258	–	–	–	–	–	–
–	–	–	–	–	–	–	–	–	–
7.1	1408	8.0	1250	–	–	6.15	1626	–	–
7.0	1429	7.95	1258	9.65	1036	–	–	8.6	1163
7.1	1408	7.95	1258	9.6	1042	–	–	8.6	1163
6.95	1439	7.95	1258	9.5	1053	–	–	–	–

SUMMARY

1. The infrared absorption spectra of several types of silico-organic compounds have been photographed.

2. On the basis of a study of these infrared spectra, a qualitative method of analysis has been worked out for silico-organic compounds which is applicable to a large class of them, in particular:

a) alkoxy- and aroxysilanes; b) alkyl- and arylalkoxysilanes; c) alkyl and arylsilanes; d) siloxanes, etc.

3. By means of certain analytical indications, it has been found possible to establish the presence of definite atomic groupings: $-CH_3$, C_6H_5-, $-CH_2-CH=CH_2$, $\equiv Si-CH_3$, –O–R, and Si–O bonds.

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COLOR REACTIONS OF CARBAZOLE, INDOLE, PYRROLE, AND SOME OF THEIR DERIVATIVES WITH BROMONITROINDANEDIONE

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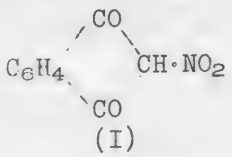
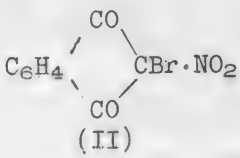
2-Nitroindanedione-1,3 (I) has already found fairly wide analytical application for the separation and identification of organic bases [1], as well as for qualitative identification of certain compounds by their color reaction with nitroindanedione [2]. One would expect that certain substituted nitroindanediones would show similar properties. It has actually been found that, e.g., a solution of carbazole in glacial acetic acid gives an intense red color with 2-bromo-2-nitroindanedione-1,3 (II). The aim of this paper is to explain the selective action and sensitivity of this reaction.



(I)



(II)

Preliminary results indicated that the intensity of the red color obtained depends partly on the concentration of carbazole, the amount of bromonitroindanedione, and the time for which the mixture is heated. It was shown that it is best to use the reagent in a dry state. Bromonitroindanedione is a colorless material; its solutions in ether, benzene, and other solvents are colorless, but its solution in glacial acetic acid is colored an intense yellow.

Increasing the amount of reagent used increases the color intensity but only up to a certain limit. Solutions boiled for 5 minutes are more intensely colored than those boiled for only 1 minute. A longer period of boiling does not lead to a further increase in intensity. The limiting concentration at which a weak rose color can still be observed is 1:500,000.

On calculating the molecular ratios, it was shown that a color can develop even when only 1 mole of bromonitroindanedione is used for 250 moles carbazole. At high dilutions a small excess of bromonitroindanedione slightly increases the color intensity, which is greatest when 2-4 moles of bromonitroindanedione are used for 1 mole carbazole. It is only when the number of moles of reagent per mole carbazole becomes greater than 8 that the sensitivity of the reaction begins to decrease.

Other solvents were tried in addition to glacial acetic acid; these included acetone, ether, dioxane, benzene, toluene, chloroform, carbontetrachloride, pyridine, methyl-, ethyl-, and isoamyl alcohols. It was only in the latter instance that a red color was obtained, but it was shown that isoamyl alcohol itself gives a red color with bromonitroindanedione. Whether or not

this is a property of isoamyl alcohol itself or of some other compound contained in it has not yet been determined. The effect of other compounds on the appearance of a color was also studied. It was found that the presence of the following organic compounds did not interfere with the color; formic, tartaric, benzoic, cinnamic, phthalic, picric, and other acids; acetophenone, benzophenone, anthraquinone, phloroglucinol, naphthalene, acetamide, acetanilide, glycerol, etc. A number of other compounds, however, interfere with the development of a red color, and only a yellow-colored solution is obtained. These compounds included phenol, pyrocatechol, resorcinol, hydroquinone, salicylic, oxalic and anthranilic acids, aniline, o-nitraniline, diphenylamine, urea, leucine, α-naphthol, formaldehyde, etc. All these reagents are known to be easily brominated, and it is possible that the reagent is thereby destroyed because it is easily converted into the nitroindanedione.

3-Nitrocarbazole and 3,6-dinitrocarbazole tested in the same way did not give a red color with bromonitroindanedione; only yellow solutions were obtained. N-acetylated carbazole did not give any characteristic color with bromonitroindanedione either; if a little carbazole is added, the red color is obtained. This reaction may therefore be used for checking the purity of N-acyl carbazoles. Since the reaction of carbazole with bromonitroindanedione is fairly sensitive, it was of interest to check this reaction with simpler analogs; i.e., with indole and its derivatives.

Indole gave a red color with bromonitroindanedione, but in contrast to carbazole, the color appears without heating and becomes more intense after a few hours. The concentration limit for indole is 1:100,000.

Calculation shows that a red color appears when there is only 1 mole reagent: 350 moles indole, while for a ratio of 1 mole reagent to 7 moles indole, the solution becomes brown on boiling the solution. This means that excess reagent should be avoided.

2-Methylindole both at ordinary temperatures and on heating gives a violet-red color with bromonitroindanedione. The limiting concentration at ordinary temperatures is 1:10,000, and on heating 1:40,000 (dirty-rose color). A large excess of reagent is to be avoided; here again, particularly on heating the solution acquires a brown color.

3-Methylindole in glacial acetic acid at a dilution of 1:1,000 gives a different color with bromonitroindanedione; the color is greenish after 1 hour but changes to blue on standing for a day. On heating, the following sequence of color changes occurs: red, red-violet, blue-violet, blue. All these changes occur in the course of 1 minute. The limiting concentration at which 3-methylindole can be detected is 1:4,000. When excess reagent is used, only an orange-yellow color is obtained.

7-Methylindole both at ordinary temperatures and on heating gives a red color with bromonitroindanedione. Excess of reagent should be avoided. Heating increases the reaction sensitivity slightly. Limiting concentration 1:40,000.

2,3-Diphenylindole gives a violet-red color under the conditions indicated. Limiting concentration 1:100,000.

Heteroauxin only gives a red color after prolonged heating. Limiting concentration 1:1,000. It is possible that heteroauxin itself does not give a positive reaction, but on heating decomposes to form indole or 3-methylindole, which reacts with the bromonitroindanedione.

Tryptophane in glacial acetic acid gives a rose color with a brownish-green fluorescence on reacting with bromonitroindanedione, while a small amount of black precipitate is formed. Excess reagent changes the color to reddish-brown and destroys the fluorescence. Limiting concentration 1:100,000.

The following amino acids were tested in parallel: glycine, α-alanine, α-aminobutyric acid, leucine, and histidine hydrochloride. All of them in glacial acetic acid give a yellow color. It can be assumed therefore that this reaction is specific for tryptophane and is more sensitive than the Miller-Lyons reaction with phenol and sodium hypochlorite or with sodium hypochlorite and hydrochloric acid [3], the sensitivity of which, according to the author, is 1:31,900.

Finally, the basic compound of this group of heterocyclics was tested, viz., pyrrole itself; this gives a reddish-violet color on heating with bromonitroindanedione in glacial acetic acid. Limiting concentration 1:10,000.

Many other nitrogen containing heterocyclic compounds which were tested only give a yellow color in glacial acetic acid on testing with bromonitroindanedione, e.g., pyridine, α-picoline, 2,4-dimethylpyridine, piperidine, conine, nicotine, quinoline, isoquinoline, benzimidazole, 3,5-dimethylpyrazole, antipyrine, caffeine, xanthine, etc.

The reaction is carried out as follows: The test material is dissolved or suspended in glacial acetic acid, a little bromonitroindanedione is added, and the mixture allowed to stand for some time or heated for a few minutes. A characteristic color is obtained in the presence of many compounds with the pyrrole ring (see table). Carbazole and heteroauxin only give a color after heating the solution; the rest give a color without heating. Heating accelerates the appearance of color and makes the reaction somewhat more sensitive. Pyrrole only gives a dirty green color without heating.

TABLE

Colors Obtained with Bromonitroindanedione in Glacial Acetic Acid

Compound	Color of solution	Limiting concentration at which a color is still observable
Carbazole	Red	1:500,000
Indole	Red	1:100,000
2-Methylindole	Red-violet	1: 40,000
3-Methylindole	Blue	1: 4,000
7-Methylindole	Red	1: 40,000
2,3-Dimethylindole	Violet-red	1:100,000
Tryptophane	Rose with brownish-green or green fluorescence (and a black precipitate down to dilutions of 1:20,000)	1:100,000
Heteroauxin	Red	1: 1,000
Pyrrole	Red-violet	1: 10,000

Note. V. Petrovska carried out some of the experimental work.

SUMMARY

2-Bromo-2-nitroindanedione-1,3 gives characteristic colors with many compounds containing the pyrrole ring in glacial acetic acid. Of major importance is the reaction with carbazole, which is the most sensitive, and that with tryptophane which is especially specific, since not one of the heterocyclic compounds tested gives this reaction; no other amino acid tested gives this reaction either.

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COLOR REACTIONS OF CERTAIN MERCURIATED AROMATIC AMINES WITH NITRITES

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Certain mercuriated secondary and tertiary aromatic amines form crystalline red or yellow compounds with nitrites in glacial acetic acid solution [1]. The intensity of the color of millimolar solutions of these compounds is greater than that of the products obtained from the respective solutions of non-mercuriated amines.

This fact agrees with the chromophore theory, according to which the change-over of a colored undissociated molecule to the ionic state (formation of organo-mercury salts) leads to a more intense color [2,3].

The present paper is devoted to the study of the reaction of mercuriated aromatic amines with nitrites, and of the possibility of using organo-mercury compounds and their synthesis for the determination of nitrites and certain secondary or tertiary aromatic amines.

Monomercuriated methyl-, ethyl-, dimethyl-, diethyl- and ethylbenzylaniline were prepared for this study, the latter being prepared in a similar manner to that given for benzylaniline [4,5].

In order to compare the nitrosation reactions, we also carried out tests with the non-mercuriated compounds, in this case the secondary aromatic amines were subjected to additional purification [6].

These reactions were carried out at 85-100° in acetic acid solution, since mineral acids decompose the organo-mercury compounds [4,5], while heating increases the color intensity of the solution. There are indications in the literature [7], of similar reactions being carried out at 40-80°.

In order to evaluate the effect of mercuriation on the intensity of the colors obtained, some of the nitrosated product was obtained as follows.

To a solution of the organo-mercury compound in 10%- and of aromatic amine in 1% acetic acid solution was added excess of sodium nitrite, and the mixture heated for 5 minutes at 85-100°. When this is done, the mercuriated compounds form crystalline products (Table 1), methylaniline – red, and dimethylaniline – a dark green oily liquid.

The nitrosation products gave blue and green colors when tested by the Lieberman reaction, thus indicating the presence of nitroso groups [7,8].

The yellow color of the solutions of the compounds obtained (at pH 4-4.5) is observable at the following concentrations, calculated in terms of the free base, for mercuriated amines – 0.35 μ g of dimethylaniline or 3.7 μ g of methylaniline, while for the non-mercuriated compounds the respective values were 1.6 or 22 μ g in 5 ml of 1% acetic acid.

When the mercuriation and nitrosation reactions were combined, microgram amounts of nitrites and certain secondary and tertiary amines could be detected. These determinations were carried out by the standard series method and photometrically, in the latter method a 436 m μ light filter was used.

Determination of Nitrites. To 4 ml of an aqueous test solution was added 1 ml of reagent (10 mg/ml of the organo-mercury compound or the corresponding amount of aromatic amine in 10% acetic acid), 1 ml of 1% acetic acid and the whole heated for 5 minutes at 85-100°. On cooling, 20% sodium acetate was added at the rate of 0.1 ml per ml of 1% acetic acid. The pH was thus raised to 4-4.5. The color develops rapidly and keeps for one month. A calibration curve was drawn up in the same way, the solutions used containing from 0.1 to 20 μ g NO_2^- in 5 ml.

TABLE 1

Characteristics of the Reaction Products of Nitrous Acid with Mercuriated Aromatic Amines

Nitrosated Compound	M.p. (°C)	Reaction product		
		M.p. (°C)	Color of crystals	Color of solution in 10% acetic acid
1,4-Methylamino-phenylmercuri-acetate	149-150	128-130, decom-poses at 181-183	Pale orange needles, rods.	Greenish-yellow to orange.
1,4-Ethylamino-phenylmercuri-acetate	128-129	125-126, decom-poses at 175	Pale yellow needles, plates.	Greenish-yellow to orange.
1,4-Dimethylamino-phenylmercuri-acetate	164-165	105-107	Orange-red plates with a metallic luster.	Greenish-yellow to red.
1,4-Diethylamino-phenylmercuri-acetate	104-105	103-104	Dark red prisms with metallic luster.	Greenish-yellow to red.
1,4-Ethylbenzyl-aminophenyl-mercuriacetate.	91- 92	No crystalline precipi-tate formed.		Greenish-yellow to red.

TABLE 2

Sensitivity of the Reactions for the Colorimetric Determination of Nitrites with Mercuriated and Non-Mercuriated Aromatic Amines

Organo-mercury compounds	NO_2^- μg/5 ml	Aromatic amines	NO_2^- μ g/5 ml
1,4-Methylaminophenyl-mercuriacetate	0.7	Methylaniline	10
1,4-Ethylaminophenyl-mercuriacetate	0.9	Ethylaniline	15
1,4-Dimethylaminophenyl-mercuriacetate	0.08	Dimethylaniline	1
1,4-Diethylaminophenyl-mercuriacetate	0.16	Diethylaniline	1.5
1,4-Ethylaminophenyl-mercuriacetate	0.1	Ethylbenzylaniline	1.5

Table 2 contains results on the reaction sensitivity, while Figs. 1 and 2 illustrate the basic characteristics of the optical properties of the colored solutions. Fig. 2 shows that the color follows the Lambert-Beer law.

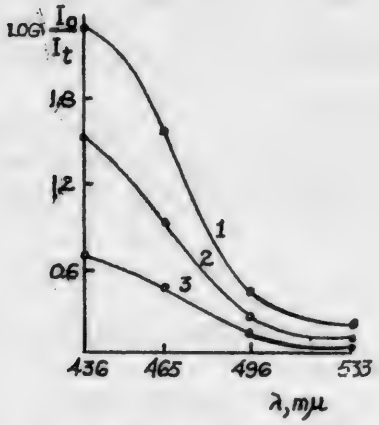

Fig. 1. Relation between light absorption and wave length for varying nitrite concentrations.
Reagent: 1,4-dimethylaminophenylacetate; 1, 2, 3, respectively at 20, 13, 6.5 μ g NO_2^-

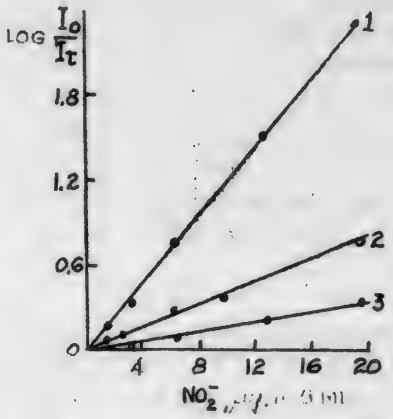

Fig. 2. Relation between color intensity at λ = 436 m μ and nitrite concentration.
1 – With 1,4-dimethylaminophenylmercuriacetate, 2 – with 1,4-methylaminophenylmercuriacetate, 3 – with dimethylaniline.

A large excess of halides, nitrates, sulfites, and sulfates, and a 25-fold excess of H_2S water has no effect on the color.

By using this reaction in reverse it is also possible to determine 1 μ g of mercuriated tertiary-, or down to 10 μ g of secondary aromatic amine in 5 ml solution.

Determination of Aromatic Amines. To 4 ml of aromatic amine solution was added 0.1 ml of mercuric acetate (15 mg/ml) solution in 1% acetic acid. A blank test was put on at the same time, no mercuric acetate being added in this case. The solution was heated for 5 minutes at 85-100°, 0.1 ml of 1% sodium nitrite was added, and the whole heated for another 5 minutes. On cooling, 0.4 ml of 20% sodium acetate was added, the solution was then mixed and determined colorimetrically. The standards used were prepared in exactly the same way, 0.5 to 25 μ g of tertiary or 4 to 20 μ g of secondary aromatic amine in 5 ml acetic acid being used. Results of reaction sensitivity are given in Table 3.

TABLE 3

Sensitivity for the Colorimetric Determination of Aromatic Amines by Means of Nitrites

Amine	μ g amine in 5 ml solution	
	With mercurization	Without mercurization
Methylaniline	4	20
Ethylaniline	5	25
Dimethylaniline	0.5	1.2
Diethylaniline	0.7	1.8
Ethylbenzylaniline	0.5	1.4

Aniline, alcohol, acetone, and a 5-10 fold excess of phenol do not interfere.

These reactions can also be used for the determination of nitrites in the absence of organomercury reagents. A solution of 20 mg mercuric acetate + 6 mg of dimethylaniline in 1 ml of 1% acetic acid heated beforehand to 85-100° can be used as a reagent. The reaction sensitivity is the same as for the organo-mercury reagents (Table 2).

These tables and figures show that mercuriation effectively increases the color intensity of the solutions during reactions between aromatic amines and nitrous acid. The greater sensitivity of the reaction with tertiary amines as compared with secondary amines can be explained by the difference in position of the chromophoric group (probably NO). Small differences in reaction sensitivity among individual members of the secondary and tertiary amines can be partly explained by kinetic factors. It is known, e.g., that the rate of interaction between nitrous acid and methylated aromatic amines is greater than with ethylated derivatives [9,10].

As compared with the method described in the literature [11, 12] the sensitivity of this reaction which we have suggested involving the use of a metallo-organic synthesis enables 0.1 μg as again 1 μg of dimethylaniline to be detected in 1 ml solution.

SUMMARY

Mercuriation of secondary and tertiary aromatic amines increases the sensitivity of colorimetric reactions with nitrites by 2.5-16 times.

By using organo-mercury reagents it is possible to determine down to 0.08 μg of NO_2^-, while using the metallo-organic synthesis, down to 0.5 μg of tertiary or 4 μg of secondary aromatic amines can be determined in 5 ml solution.

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ABSORPTION OF SULFUR OXIDES BY METAL OXIDES AND SILICATES

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The use of solid absorbents for taking up sulfur oxides was fairly common in the early development of organic analysis. The following absorbents have been suggested at various times: cupric oxide [1], asbestos + lead dioxide [2], calcium oxide [3], lead chromate, silver vanadate, metallic silver, and others.

At present, solid absorbents, with the exception of metallic silver, are hardly used at all for the quantitative determination of sulfur in organic materials. Lead dioxide and lead chromate are often used for taking up the sulfur in carbon-hydrogen estimations.

Numerous papers have been devoted to the application of metallic silver for absorption of sulfur oxides and halogens, but mainly in the field of microelemental analysis. The absorption of sulfur oxides by silver at high temperatures has been successfully used in the method developed by M. O. Korshun and N. S. Sheveleva [4], and described in a monograph [5].

Our aim was to study the possibility of replacing silver by other more readilyaccessible materials. During this study absorption of sulfur oxides by metal oxides and silicates was investigated. Sulfur is determined by the increase in weight of absorbent.

Solid absorbents can be used for the analysis of organic compounds containing not only C, H, O, and S, but C, H, O, S, and N, since at temperatures of 700-800° the gaseous reaction products contain only the indifferent oxide of nitrogen, nitric oxide, which does not react with the absorbent. Consequently it is best to keep the temperature at which the reaction between sulfur oxides and absorbent is going to occur within the limits of 700-800°. Reactions between sulfur oxides and metal oxides or silicates proceed as follows:

$$MeO + SO_3 = MeSO_4;$$

$$Na_2SiO_3 + SO_3 = Na_2SO_4 + SiO_2.$$

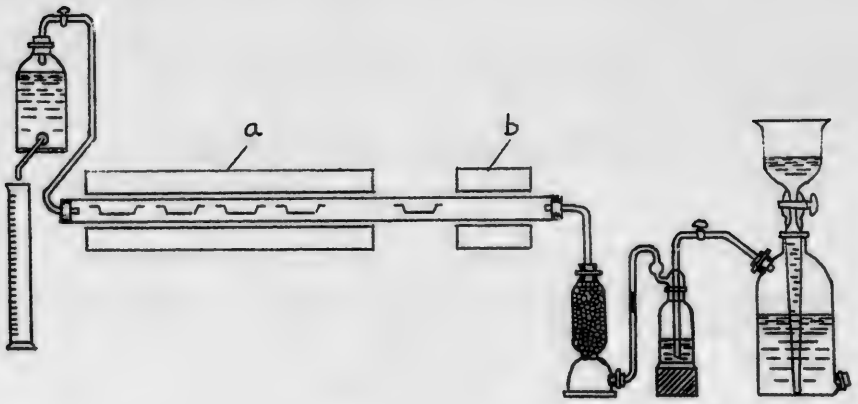
From which the conversion factor is —

$$\frac{S}{SO_3} = 0.40049 \sim 0.4005;$$

which is slightly less than the factor for silver $\frac{S}{SO_4} = 0.3338$.

Principle of the Method

Quantitative determination of sulfur in organic compounds by absorption with solid absorbents consisted in combustion of the sulfur-containing material in an empty tube at 800° in the presence of chromic oxide as a catalyst, this being sprinkled over the aliquot of test material contained in a boat. The sulfur oxides formed were absorbed at 700-800° with solid absorbents placed in boats in the combustion tube. The oxygen throughput was 50 ml/minute. Sulfur content was determined by the increase in weight of the boat. The apparatus is depicted in the diagram.



Preparation for Analysis

The absorbent was first of all calcined in a muffle at 600-800° for 3-4 hours, according to the type of absorbent used. Before analysis the absorbent was placed in a porcelain boat, which was then introduced into the combustion tube and heated for 1-2 hours in a stream of oxygen running at 50 ml/minute. The boat and contents were then removed from the tube and placed in a test tube fitted with a ground glass stopper, and the whole kept in a desiccator. The tube was allowed to cool for 20-30 minutes. The test tube was then closed and weighed.

The following oxides were tested as absorbents for sulfur oxides: magnesium oxide, cupric oxide, lead dioxide, cadmium oxide and sodium silicate.

Blank tests were carried out beforehand in order to establish the change in weight of absorbent which occurs during calcining in the tube in a stream of oxygen. The throughput was varied. The results obtained for some of the absorbents are adduced in Table 1.

These results show that an increase in oxygen throughput leads to losses in weight of the absorbent as a result of carry-over of particles as shown by the large differences in weight in the blank tests. Pressing some of the oxides leads to a decrease in this loss of weight, but does not prevent it. Optimal results were obtained in the blank tests when sodium silicate was used, presumably because its particles are heavier than those of the other absorbents tried. Changes in weight of sodium silicate during combustion of saccharose in blank tests are given in Table 2.

The variations in weight of absorbent are appreciable because of the carry-over of absorbent particles and deflagration of the compound at such a low oxygen throughput.

In order to illustrate the capacity of silicate to absorb moisture and carbon dioxide from the air, results are adduced for increases in weight of silicate on leaving it in the open air in boats.

After 2 hours	0.02 g
After 24 hours	0.08 g

Experimental Procedure

Four boats containing preliminarily calcined and weighed sodium silicate were placed in the combustion tube. The aliquot of sulfur containing material

TABLE 1

Material	Weight, in g: Before calcining	Weight, in g: After calcining	Difference	Oxygen throughput, in ml/min	Temperature, in °C
Sodium silicate	63.1184	63.1185	+0.001	50	
	63.1185	63.1180	−0.0005	50	
	69.6595	69.6595	−0.0001	50	
	69.6594	69.6594	0.0000	50	800
	70.4050	70.4042	−0.0008	75	
	70.4042	70.4052	+0.0010	75	
	81.3146	81.3140	−0.0006	75	
	81.3140	81.3134	−0.0006	75	
Cadmium oxide, pressed	84.5488	84.5440	−0.0048	50	700
	83.7120	83.7058	−0.0062	50	
Magnesium oxide, unpressed	73.7108	73.6912	−0.0196	50	800
	75.9074	75.8894	−0.0080	50	
Magnesium oxide, pressed	75.8132	75.8070	−0.0052	50	
	74.5372	74.5343	−0.0029	50	
	75.8064	75.8044	−0.0020	50	800
	74.5424	74.5372	−0.0052	50	
	74.5372	74.5347	−0.0025	50	
	75.8058	75.8020	−0.0038	50	

TABLE 2

Absorbent	Weight, in g: Before combustion	Weight, in g: After combustion	Difference	Oxygen throughput, in ml/min
Sodium silicate	72.7828	72.7844	+0.0016	50
	81.7186	81.7170	−0.0016	50
	77.6832	77.6818	−0.0014	50
	87.3109	87.3094	−0.0015	50

(0.1000-0.1500 g) also in a boat was strewn with chromic oxide and placed in the tube at a distance of 3 cm from the part of the oven heated to 700-800°. Immediately on putting the boat plus aliquot in position the second electric oven between the aliquot and purifying system was switched on; the idea of the purifying system is to prevent a reverse distillation of the test material. The oxygen from the gas-holder was passed through a purifying system containing alkali. As soon as the temperature in the little electric oven had reached 700-800°, it was moved on to a quarter of the boat + aliquot gradually, and then in the course of 10-15 minutes on to the whole of the length of the boat. The boat was heated for 5 minutes and oxygen passed for another 15 minutes in order to ensure complete removal of the gaseous products. The boat was then removed from the tube, placed in an open test tube, and left in a desiccator; the whole was cooled for 25-30 minutes and weighed.

Tests showed that cupric oxide is not a suitable absorbent for the quantitative determination of sulfur because of the low temperature at which the sulfate which is formed decomposes. Lead dioxide under the experimental conditions employed changed color from yellow to red, indicating formation of red lead,

so that this oxide is unsuitable as an absorbent also. Cadmium oxide is similarly inapplicable, since there is a considerable loss in weight during blank tests; in addition their reactivity is low.

Magnesium oxide is fairly reactive, but the drawback in this case is the large carry-over of particles with the oxygen stream, as is shown by considerable losses in weight in the blank tests.

Near quantitative results for the quantitative determination of sulfur in organic compounds were obtained with sodium silicate as absorbent; results of these determinations are given in Table 3. They indicate that sodium silicate is a potential substitute for metallic silver.

TABLE 3

Absorbent	Substance and empirical formula	Weight of aliquot, in g	Increase in weight, in g	Sulfur in % Found	Sulfur in % Calculated	Difference	Absorption temp., in °C
Na_2SiO_3	p-Toluenesulfamide $C_7H_9SO_2N$	0.1142	0.0514	18.02	18.71	−0.69	800
		0.0966	0.0465	19.27	18.71	+0.56	
	Phthalsulfothiazole $C_{16}H_{13}O_5N_3S_2$	0.1310	0.0506	15.46	15.89	−0.43	800
		0.1476	0.0509	15.43	15.89	−0.46	
	4-Sulfanilylsulfanilamide $C_{12}H_{13}O_4N_3S_2$	0.1176	0.0556	18.93	19.59	−0.66	800
		0.1278	0.0602	18.87	19.59	−0.73	
	Thiosemicarbazide CH_5N_3S	0.1168	0.1030	35.31	35.17	+0.14	800
		0.1219	0.1061	34.85	35.17	−0.32	
	Sulfosalicyclic acid $C_7H_6SO_6 \cdot 2H_2O$	0.1119	0.0367	13.13	12.61	+0.52	800
		0.1530	0.0475	12.43	12.61	−0.18	
		0.1930	0.0614	12.74	12.61	+0.13	
MgO, pressed	Ditto	0.1000	0.0290	11.61	12.61	−1.00	700
		0.1552	0.0500	12.90	12.61	+0.29	
	4-Sulfanilylsulfanilamide	0.1102	0.0510	18.53	19.59	−1.06	700

Slight deviations within the limits of 0.5% in the results for sulfur content on absorption of sulfur oxides with sodium silicate are the results of a small carry-over of absorbent with the oxygen stream. It would be natural to expect that exact quantitative results are possible if a form of absorbent apparatus is used in which the absorbent itself is in the form of a tube connected to the combustion tube. This type of absorbent apparatus would prevent the loss of particles by carry-over with the oxygen stream. We managed to prove this by carrying out some analyses in such an apparatus [4] which was given to us by the Microanalytical Laboratory of the Institute of Organic Chemistry.

The results of these tests are given in Table 4 from which it is possible to conclude that sodium silicate can be used as an absorbent instead of metallic silver in elemental analysis for quantitative absorption of sulfur oxides.

SUMMARY

1. Absorption of sulfur oxides by metal oxides and silicates has been studied.

TABLE 4

Absorbent	Sample	Weight of sample, in g	Increase in weight, in g	Sulfur, in %		Difference
				Found	Calculated	
Sodium silicate	o-Toluene sulfamide	0.1238	0.0570	18.43	18.71	−0.28
		0.1224	0.0564	18.45	18.71	−0.26
	Sulfosalicylic acid	0.1592	0.0492	12.37	12.61	−0.24
		0.1025	0.0320	12.50	12.61	−0.11
	Naphthionic acid	0.1118	0.0386	13.82	13.81	+0.01
		0.1082	0.0367	13.58	13.81	−0.23
	2-/p-Aminobenzenesulfamidopyridine	0.0731	0.0228	12.60	12.86	−0.26
		0.0952	0.0302	12.70	12.86	−0.16

2. It has been shown experimentally that metallic silver can be replaced in organic analysis by more readily accessible materials, such as metallic oxides and silicates.

3. The best results were obtained with sodium silicate which rapidly and quantitatively absorbs sulfur oxides.

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IODOMETRIC DETERMINATION OF CADMIUM

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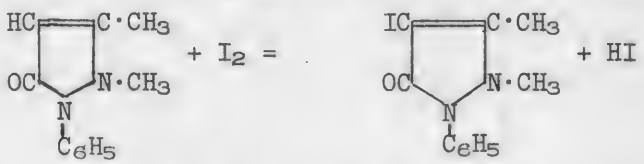
In our previous paper [1], it was shown that cadmium can be determined quantitatively by several methods including the diantipyrylorthohydroxyphenylmethane method; cadmium is also precipitated quantitatively in acid media by antipyrinebromide reagent, a compound of the following composition being obtained [2]:

$$[C_{11}H_{12}ON_2H]_2[CdBr_4]\cdot 2C_{11}H_{12}ON_2.$$

The volumetric method for the quantitative determination of antipyrine is based on the fact that it gives iodopyrine with iodine:



The residue taken in excess iodine solution is titrated with sodium thiosulfate. In view of the reversibility of the formation of iodopyrine, it is essential to add sodium acetate to take up the hydrogen iodide. Knowing how much iodine has been used for the formation of iodopyrine it is possible to calculate the amount of cadmium.

The iodometric method of determining cadmium was worked out initially on pure cadmium salts.

Cadmium solutions were prepared by dissolving 1 g metallic cadmium in nitric acid, and the solution diluted to 200 ml with water. 1 ml solution contains 5 mg cadmium. This was checked electrolytically.

EXPERIMENTAL

The antipyrinebromide reagent was prepared as follows: 10 g of potassium bromide and 5 g antipyrine were dissolved in 85 ml of 0.25 N sulfuric acid. An excess of this reagent was added to the test cadmium solution. Turbidity or a precipitate developed according to the amount of cadmium present. After rubbing with a glass rod (15-20 seconds) the precipitate rapidly changed into a crystalline form. After 30-35 seconds the precipitate was filtered through a number 4 sintered glass crucible; the filtrate was used for completely transferring all the precipitate onto the filter. The precipitate was washed once or twice with a small amount of dilute (1:1) solution of the antipyrinebromide reagent, and then, without giving it a chance to dry out, washed off the filter with 25-30 ml of water into a flask fitted with a ground-glass stopper. If the precipitate should adhere closely to the bottom of the crucible, it should be loosened first with a glass rod fitted with a rubber policeman. Tests indicated that the precipitate need not be washed with the antipyrinebromide reagent; results in this case are somewhat higher but not too high.

After the precipitate had been washed, 3 g of sodium acetate was added followed by 25-30 ml of 0.1 N iodine solution. The flask was then stoppered and the liquid thoroughly shaken; immediately or sometime after, a precipitate

was formed which appeared in the shape of dark brown colored threads. After 30-40 minutes, from 25-50 ml of ethyl alcohol was added until all the precipitate dissolved, and the excess iodine back titrated with 0.1 N sodium thiosulfate.

1 ml of 0.1 N iodine is equal to 1.405 mg cadmium.

Results of tests are adduced in Table 1.

TABLE 1

Amount of cadmium, in mg	Amount of antipyrine bromide reagent added, in ml	Amount of 0.1 N iodine added, in ml	ml of 0.1 N sodium thiosulfate used in titrating iodine	Amount of 0.1 N iodine used to form iodopyrine, in ml	Cadmium found, in mg	Absolute error, in mg
5	5	25	21.38	3.62	5.09	+0.09
10	10	50	42.87	7.13	10.02	+0.02
15	15	50	39.21	10.79	15.15	+0.15
15	15	25	14.36	10.64	14.95	−0.05
20	20	50	39.95	14.05	19.74	−0.26
20	20	25	10.95	14.05	19.74	−0.26
25	25	25	7.1	17.9	25.15	+0.15
25	25	50	32.41	17.59	24.71	−0.29
25	25	50	31.92	18.08	25.4	+0.4

The results obtained are satisfactory.

This iodometric method for cadmium was checked in the presence of other salts. Solutions of cupric chloride ($CuCl_2 \cdot 2H_2O$) and magnesium sulfate ($MgSO_4 \cdot 7H_2O$) of varying concentrations were used and known amounts of cadmium solution added to them. For each ml of the mixture thus obtained ca. 2.5-3 ml of the antipyrinebromide reagent was required for precipitation of cadmium, and in each case 25 ml of 0.1 N iodine solution was used.

The results are adduced in Table 2.

TABLE 2

Amount of cadmium, in mg	Amount of other salts, in g		Cadmium found, in mg	Absolute error, in mg
5	0.25	$CuCl_2 \cdot 2H_2O$	4.95	−0.05
5	0.25	$CuCl_2 \cdot 2H_2O$	5.06	+0.06
10	0.25	$CuCl_2 \cdot 2H_2O$	10.13	+0.13
15	0.25	$CuCl_2 \cdot 2H_2O$	14.89	−0.11
20	0.25	$CuCl_2 \cdot 2H_2O$	19.67	−0.33
25	0.25	$CuCl_2 \cdot 2H_2O$	24.38	−0.66
15	0.5	$CuCl_2 \cdot 2H_2O$	15.02	+0.02
20	0.5	$CuCl_2 \cdot 2H_2O$	19.91	−0.09
10	0.25	$MgSO_4 \cdot 7H_2O$	10.16	+0.16
15	0.25	$MgSO_4 \cdot 7H_2O$	15.02	+0.02

This method was used for the determination of cadmium in various alloys, such as Elektron, which contains magnesium, aluminum and zinc, and iron-aluminum alloy, which contains copper, iron, aluminum, zinc and manganese; in both cases the cadmium was added artificially.

ANALYTICAL PROCEDURE

1 g of Elektron was dissolved in sulfuric acid (1:10). 1 g of the bronze was dissolved in 10 ml dilute (1:1) nitric acid, and after evaporation on a water bath, 50 ml water was added. Excess antipyrinebromide reagent was added to known volumes of the solutions of these two respective alloys containing a known weight of cadmium; subsequent procedure was as outlined above.

Analytical results are given in Table 3.

TABLE 3

Amount of cadmium added, in mg	Amount of cadmium found, in mg	Absolute error, in mg.
Elektron alloy		
10	10.6	+0.6
10	10.19	+0.19
15	15.17	+0.17
20	20.02	+0.02
25	24.94	−0.06
Ironaluminum bronze		
15	14.77	−0.23
20	20.44	+0.44
20	19.6	−0.4
25	24.38	−0.62

TABLE 4

Amount of cadmium taken, in mg	Amount of cadmium found, in mg	Absolute error, in mg.
10	10.23	+0.23
12.5	12.25	−0.25
12.5	12.25	−0.25
15	14.61	−0.39
17.5	17.14	−0.36
20	20.18	+0.18

TABLE 5

Amount of cadmium taken, in mg	Amount of other salts, in g		Amount of cadmium found, in mg	Absolute error, in mg
10	1	$MgSO_4 \cdot 7H_2O$	9.95	−0.05
15	1	$MgSO_4 \cdot 7H_2O$	14.89	−0.11
10	0.5	$CuCl_2 \cdot 2H_2O$	9.95	−0.05
15	0.5	$CuCl_2 \cdot 2H_2O$	15.06	+0.06
5	0.25	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ + 0.25 $CoCl_2 \cdot 6H_2O$	4.95	−0.05
10	0.25	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ + 0.25 $CoCl_2 \cdot 6H_2O$	9.95	−0.05
15	0.25	$(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$ + 0.25 $CoCl_2 \cdot 6H_2O$	15.17	+0.17

These results show that the antipyrinebromide- iodometric method for determination of cadmium gives completely satisfactory results. The relative experimental error varies within the limits ±3%.

Further experiments showed that cadmium could be successfully determined by a saturation method.

If alkali is allowed to react with the precipitate, $[C_{11}H_{12}ON_2]_4H_2[CdBr_4]$, formed after addition of the antipyrinebromide reagent to solutions of cadmium salts, then the hydrogen ions are neutralized. The method of precipitating cadmium remains the same as during the iodometric method. The precipitates are washed from the glass crucible with 50 ml water into a 250-300 ml flask. The solution in the flask is then gently heated to dissolve all the precipitate,

the solution formed is then diluted to 150 ml with water and titrated with 0.1 N alkali in the presence of 5 drops of methyl orange. 1 ml 0.1 N NaOH corresponds to 5.62 mg cadmium. The first tests were carried out with pure cadmium salts (see Table 4).

Cadmium was subsequently determined in the presence of other salts; magnesium and nickel sulfates, copper and cobalt chlorides. Analytical results are adduced in Table 5.

Finally cadmium was determined by this method in the presence of other metals in the two alloys Elektron and Ironaluminum bronze, the cadmium itself had to be added artificially to the alloys (see Table 6).

TABLE 6

Amount of cadmium added, in mg	Amount of cadmium found, in mg	Absolute error, in mg
Elektron alloy		
10	10.12	+0.12
20	20.23	+0.23
Ironaluminum bronze		
10	9.84	−0.16
15	14.61	−0.34

These results show that the saturation method gives satisfactory results for the determination of cadmium.

SUMMARY

1. Two volumetric methods have been worked out for the determination of cadmium — an iodometric one and a neutralization method, both based on the use of antipyrinebromide reagent.

2. By means of both these methods cadmium can be determined in the presence of magnesium, copper, zinc, cobalt and other metals.

3. The relative experimental error varies within the limits ±3%.

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IODOMETRIC DETERMINATION OF ARSENIC ACID USING ORGANIC SOLVENTS

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The first stage of the reversible oxidation of iodides by arsenic acid can be expressed by the following equation:

$$H_3AsH_4 + 2I^- + 2H \rightleftharpoons H_3AsO_3 + H_2O + I_2. \qquad (1)$$

This reaction has been studied by many authors [1-8] with the aim of choosing conditions such that it will go completely from left to right and can then be used for the quantitative iodometric determination of arsenic acid. It has been found that in strong acid media the equilibrium is displaced from left to right to quite an appreciable extent, but on the other hand under these conditions titration of the strong acid solution with sodium thiosulfate is not easy. Thus if the solution is diluted before titration in order to decrease the effect of the strong acid medium on the sodium thiosulfate, this will also favor the right-to-left process in reaction (1). The use of a large excess of iodide is accompanied by large errors as the result of oxidation by atmospheric oxygen. Finally it should be noted that ions of iron (III), manganese, molybdate, tungstate, and other catalysts do not, according to published results, show an appreciable effect on the reaction velocity.

The problem of a direct iodometric determination of arsenic acid thus remains open. We were particularly interested in this question as a basis for a possible arsenate method of determining many metals which are capable of forming arsenates of low solubility. On the basis of detailed investigations we succeeded in developing a method for the iodometric determination of arsenic acid in strong acid media and in the presence of a small excess of iodide, based on displacing the equilibrium in reaction (1) from left to right by extracting the iodine formed with organic solvents.

The Use of Organic Solvents in Aqueous Media with Normal pH

On the basis of equation (1) by the law of mass action:

$$\frac{[H_3AsO_4]}{[H_3AsO_3]} = \frac{[I_2]}{[H^+]^2 \cdot [I^-]^2} \cdot K \qquad (2)$$

From this expression it readily follows that the ratio of the concentrations of arsenic and arsenous acids should vary in accordance with the completeness of iodine extraction by the organic solvents. According to the distribution law of iodine between the aqueous phase and organic solvent:

$$[I_{2\,\text{aqueous phase}}] = K_{\text{partition}} \times [I_{2\,\text{organic solvent}}] \qquad (3)$$

Since the solubility of iodine in certain organic solvents is many times (100-1000 times) greater than that in water, then for the reduction of arsenic acid according to equation (1), it is possible to write:

$$[I_{2\,\text{organic solvent}}] \cdot V_{\text{organic solvent}} \approx [H_3AsO_3] \cdot V_{\text{aqueous phase}} \quad (4)$$

It must be remembered that according to equation (1), the total number of iodine mols formed is equal to the number of mols of arsenous acid formed.

From equation (4)

$$[I_{2\,\text{organic solvent}}] \approx \frac{[H_3AsO_3] \cdot V_{\text{aqueous phase}}}{V_{\text{organic solvent}}}$$

for

$$V_{\text{aqueous phase}} = V_{\text{organic solvent}}$$

we have

$$[I_{2\,\text{organic phase}}] = [H_3AsO_3],$$

Substituting this in equation (3), we have

$$[I_{2\,\text{aqueous phase}}] = K_{\text{partition}} \cdot [H_3AsO_3]. \quad (5)$$

Substituting the value of $[I_{2\,\text{aqueous phase}}]$ from equation (5) in equation (2), we get

$$\frac{[H_3AsO_4] \cdot [H^+]^2 \cdot [I^-]^2}{[H_3AsO_3]^2 \cdot K_{\text{partition}}} = K$$

or

$$\frac{[H_3AsO_4] \cdot [H^+]^2 \cdot [I^-]^2}{[H_3AsO_3]^2} = K \cdot K_{\text{partition}} = K_1. \quad (6)$$

Thus the use of organic solvents for removing iodine (should) changes the equilibrium constant in proportion to the value of the partition coefficient of iodine between aqueous phase and organic solvent:

$$K_1 = K \cdot K_{\text{partition}} \quad (7)$$

where K_1 – is the equilibrium constant when a given organic solvent is used; K – the equilibrium constant when no organic solvent is used; $K_{\text{partition}}$ – is the partition coefficient of iodine between water and the organic solvent used.

From calculations based on equation (7) and the respective partition coefficients of iodine [10], we compiled Table 1.

TABLE 1

Organic solvent	$K_{\text{partition}}$ Partition coefficient at 25°	Equilibrium constant when no organic solvent is used K	Equilibrium constant when organic solvent is used K_1
Carbon tetrachloride	0.0111	$7 \cdot 10^{-2}$	$7.8 \cdot 10^{-4}$
Chloroform	0.005		$3.5 \cdot 10^{-4}$
Carbon bisulfide	0.0009		$6.3 \cdot 10^{-5}$
Benzene	0.0008		$5.6 \cdot 10^{-5}$

These results show that the equilibrium constant of the reduction of arsenic acid with iodine changesby as much as 2-3 times according to the organic solvent used. This is of great importance for other similar reversible reactions.

According to extraction theory, the bigger the

volume of solvent used, the more complete the extraction. On the other hand, the use of a given amount of solvent in small portions gives much better results than one extraction with the same total volume of extraction agent. Nevertheless repeated extractions followed by a separation of the organic solvent layer each time are accompanied by certain losses which complicate the method and draw out the time of extraction. We decided therefore on one extraction without separation of the layer of organic solvent. As a consequence, in order to achieve as complete a displacement of the equilibrium as possible, we had to resort to the use of the largest possible volume of solvent.

According to equations (3) and (4):

$$[I_{2\,\text{aqueous phase}}] \approx K_{\text{partition}}[H_3AsO_3]\,\frac{V_{\text{aqueous phase}}}{V_{\text{organic solvent}}}$$

On substituting this value in equation (2), we get:

$$\frac{[H_3AsO_4]\cdot[H^+]^2\cdot[I^-]^2\cdot V_{\text{organic solvent}}}{[H_3AsO_3]\cdot V_{\text{aqueous phase}}} = K\cdot K_{\text{partition}} = K_1 \qquad (8)$$

This equation is more general than equation (6).

From equation (8) it follows that the completeness of reduction of arsenic acid to arsenous acid depends on the ratio of the volumes of organic solvent and aqueous phase.

As titration proceeds the iodine shifts from the organic solvent layer to the aqueous phase and reacts with sodium thiosulfate because the latter is insoluble in the organic solvents used.

The reaction between iodine and sodium thiosulfate is not appreciably reversible, so that a decrease in iodine concentration according to the partition coefficient of the latter between aqueous phase and the organic solvent used does not affect (or has practically no effect) on the accuracy of the titration. As titration of the iodine found in the organic solvent layer proceeds, it will pass over into the aqueous phase. When, however, a very large volume of organic solvent is used, this reverse movement of iodine into the aqueous phase will be made more difficult, so that the titration time will be longer drawn out.

Titrations in which various amounts of different solvents (chloroform, benzene, etc.) were used and a parallel series of titrations in which no solvents were used showed that organic solvents do displace the equilibrium in reaction (1) considerably, and that a volume of solvent equal to that of the aqueous phase is optimal. In macro titrations, chloroform and benzene can be used with equal success while for micro titrations (particularly at low concentrations) benzene is preferable since it is the best solvent and the most sensitive indicator.

For media 1 N with respect to acid the reaction is not complete immediately after mixing the reagents; consequently solutions with lower pH are better.

The Use of Organic Solvents at Low pH

Table 2 contains results of calculation (on the basis of equations 7 and 8) of the completeness of reduction of arsenic acid expressed by the ratio $\frac{[H_3AsO_4]}{[H_3AsO_3]}$, in relation to hydrogen ion concentration both with and without use of solvent; the respective experimental errors are also included, expressed as percentages, when working with 0.1 N solutions.

These results show that the experimental error in the tests in which no organic solvent is employed changes from 1.38 to 0.05% on changing the hydrogen ion concentration from 1 to 5.

TABLE 2

Expt. No.	$\frac{[H_3AsO_4]}{[H_3AsO_3]}$ when equilibrium is established			Error in %		
	When no organic solvent is used	When chloroform is used	When benzene is used	When no organic solvent is used	When chloroform is used	When benzene is used
1	$1.4 \cdot 10^{-2}$	$1.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-5}$	1.38	0.014	0.0014
2	$3.5 \cdot 10^{-3}$	$3.5 \cdot 10^{-5}$	$3.5 \cdot 10^{-6}$	0.35	0.0035	0.00035
3	$1.56 \cdot 10^{-3}$	$1.56 \cdot 10^{-5}$	$1.56 \cdot 10^{-6}$	0.15	0.0015	0.00015
4	$9 \cdot 10^{-4}$	$9 \cdot 10^{-6}$	$9 \cdot 10^{-7}$	0.09	0.0009	0.00009
5	$5.6 \cdot 10^{-4}$	$5.6 \cdot 10^{-6}$	$5.6 \cdot 10^{-7}$	0.05	0.0005	0.00005

When chloroform was used even for 1 N media the error was only 0.014%, while at $[H^+] = 4$, the error was less than the 0.001%. When benzene was used, the error was ten times less.

We studied the effect of sulfuric acid as well as hydrochloric concentration on reaction velocity (1) when organic solvents were used. From these results it was established that in order to complete the oxidation of iodide by arsenic acid, it is essential that immediately after mixing the reagents, the solution should be at least 5 N with respect to hydrochloric acid and 8 N sulfuric acid.

A further series of experiments, the results of which are not adduced for reasons of space, established that when these concentrations of the respective acids are used, results which are in good agreement with each other are only obtained when titration is carried out strictly dropwise. If large amounts of thiosulfate are added, decomposition of the latter occurs in the strong acid media. As a result the solution is diluted before titration after completion of oxidation of iodide by arsenate. This permits rapid titration which obviates decomposition of the sodium thiosulfate, while the reverse reaction of equation (1) is not observed because of the extraction of iodine by the solvent. It is sufficient to dilute to 3 N hydrochloric acid or 4 N sulfuric acid by addition of an equal volume of distilled water.

The Effect of the Amount of Potassium Iodide Used

The iodine which is evolved during reaction (1) reacts with excess potassium iodide as follows:

$$I_2 + KI \rightleftharpoons KI_3$$

or in ionic form

$$I_2 + I^- \rightleftharpoons I_3^- \qquad (9)$$

By combining equations (1) and (9), we get:

$$H_3AsO_4 + 2H^+ + 3I^- \rightleftharpoons H_3AsO_3 + H_2O + I_3^- \qquad (10)$$

Iodine dissolves as molecules of I_2 in the organic solvents we used, while the iodide and triiodide do not dissolve in these solvents. Accordingly the equilibrium in equation (9) is displaced to the left.

The extent of this displacement depends on the completeness of extraction of iodine, i.e., on the partition coefficient of iodine between aqueous phase and organic solvent. The partition coefficient in turn depends on iodide concentration. At low concentrations, and when such solvents as benzene, carbon bisulfide, chloroform, etc., are used, this equilibrium is almost completely displaced to the left. We are of the opinion therefore that when organic sol-

vents are used, the reduction of arsenic acid by iodide is more correctly expressed by equation (1). It follows from this that a displacement of equilibrium to the side of the reduction of arsenic acid when working without organic solvents is proportional to the third power of the iodide concentration, while when solvents are used, it is proportional to the second power of this concentration. [See equations (1) and (10).]

It must be emphasized that when organic solvents are used in order to displace the equilibrium (1) an increase in iodide concentration will hinder a more complete extraction of iodine from the aqueous phase and consequently interfere with the displacement of equilibrium by the solvent.

In view of this the addition of the normally recommended large excess of iodide loses its point when organic solvents are used. On the contrary it is essential that the least possible excess of iodide be used (even more so in that addition of a large excess of iodide leads to additional errors and to results which do not agree with each other as a result of the instability of potassium iodide). This fact considerably enhances the value of the use of organic solvents.

On the other hand, the use of excess iodide is significant for speeding up reaction (1). In this connection we carried out some tests on the variation of reaction velocity with iodide concentration, while chloroform was used in sulfuric acid as well as in hydrochloric acid media. It was thereby established that the optimal amount of iodide should be a twofold excess in comparison with the stoichiometrically calculated amount.

An Iodometric Determination of Arsenic Acid Using Organic Solvents

To 10 ml of test solution contained in a 150-200 ml Erlenmeyer flask was added 10-12 ml of sulfuric acid (1:1) or an equivalent concentration of hydrochloric acid. To the mixture obtained was added an equal volume of chloroform or benzene (20 ml) and 3 ml of a 1.0 N solution of potassium iodide. When working with solutions of arsenate of greater strength than 0.1 N, the concentration of potassium iodide should be increased accordingly. The mixture is shaken for a few seconds in order to extract the iodine with the layer of organic solvent and to complete the reaction, an equal volume of water is then added and the solution titrated with sodium thiosulfate. At the end point when the layer of solvent has attained a weak rose color it is necessary to shake the mixture for a few seconds after the addition of each drop of thiosulfate.

Since the effect of oxidation by atmospheric oxygen becomes rather pronounced during micro titrations, carbon dioxide should be used to expel the air. Carbon dioxide is passed for ca. 1 minute into the flask over the surface of the solution before adding potassium iodide.

Results of macro- and micro-titrations are given in Table 3.

Titration in hydrochloric acid gives results which are just as accurate and reproducible as in sulfuric acid. Micro-titrations gave good results at arsenate concentrations down to 0.001 N. At lower concentrations good results can still be obtained if a blank is carried out and the air is carefully removed by passing carbon dioxide after addition of each reagent, and repeatedly passing it during the actual titration.

TABLE 3

Conc. of arsenate solution	Volume, in ml: Arsenate	Sulfuric acid 1:1	Solvent	Volume, in ml, conc. in N of potassium iodide solution	Volume, in ml of water for dilution	Amount of thiosulfate solution used in ml	Theoretical amount of thiosulfate used in ml	Deviation, in ml
0.2	10	10	20	3 ml 2 N	20	9.95	9.98	0.03
0.1	5	5	10	1.5 1	10	5.15	5.12	0.03
0.1	10	10	20	3 1	20	10.15	10.24	0.01
0.1	15	15	30	4.5 1	30	15.35	15.36	0.01
0.1	25	25	50	7.5 1	50	25.55	25.60	0.05
0.05	10	10	20	3 1	20	10.05	10.04	0.01
0.02	10	10	20	3 1	20	10.45	10.43	0.02
0.01	1.000	1.0	2.0	0.3 1	2.0	1.030	1.028	0.002
0.01	1.000	1.0	2.0	0.3 1	2.0	1.025	1.028	0.003
0.005	1.000	1.0	2.0	0.3 1	2.0	0.990	0.992	0.002
0.005	1.000	1.0	2.0	0.3 1	2.0	1.000	0.992	0.008
0.001	1.000	1.0	2.0	0.3 1	2.0	1.150	1.139	0.011
0.001	1.000	1.0	2.0	0.3 1	2.0	1.135	1.139	0.004
0.0001	5.000	5.0	10	1.5 1	10	0.520	0.515	0.005
0.0001	5.000	5.0	10	1.5 1	10	0.530	0.515	0.015

SUMMARY

Macro- and micro-methods have been developed for the accurate and direct iodometric determination of arsenic acid based on the displacement of the reaction equilibrium by using organic solvents to remove iodine.

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QUANTITATIVE DETERMINATION OF SODIUM AS ANTIMONATE

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Among the methods of determining sodium as antimonate mention should be made of that proposed by Vinogradov and Dundur [1], by means of which sodium can be determined if the ratio of KCl:NaCl is not greater than 2:1. In order to remove excess KCl the authors adopted the original method of treating the mixture of KCl and NaCl with ethyl alcohol; when this was done, they got a ratio of KCl:NaCl equal to 1:1 in the sodium enriched solution. In order to get such a ratio for these salts, it is ssential that the amount of NaCl in the test mixture should be ca. 0.1 g.

The aim of the work described below was to work out a similar micro method by means of which it would be possible to determine one tenth of a milligram of sodium in natural products, e.g., in plants, in the presence of large amounts of potassium.

Conditions for the Formation of Large Crystals

Previous authors [1,3,4] precipitated sodium as antimonate as follows:

To the test aqueous solution of the alkaline metals was added an aqueous neutral or alkaline solution of potassium antimonate followed by 96% ethyl alcohol to secure a more complete precipitation of sodium. When this is done, as Vinogradov and Dundur pointed out, exceedingly fine crystals are obtained which can pass through a filter, and therefore complicate filtration. When this method of precipitating sodium is employed, at the moment when the alcohol comes into contact with the mixture of solution, not only formation of a fine precipitate occurs as a result of local supersaturation, but at certain ratios of KCl, $KSb(OH)_6$, and alcohol, precipitation of reagent also occurs.

On the basis of tests connected with the crystallization process of $NaSb(OH)_6$, we established that in order to form a coarse, rapidly settling precipitate, it is essential to prepare an alcoholic solution of reagent and add it to an alcoholic solution of the mixture of NaCl and KCl. This should be carried out at 0° for 30-60 minutes in order to ensure complete precipitation of sodium.

The Optimal Concentration of $KSb(OH)_3$ in the Original Solutions

There does not seem to be unanimous agreement in the literature as to the composition of solutions of $KSb(OH)_6$ used for quantitative precipitation of sodium. Vinogradov and Dundur showed that a freshly prepared saturated aqueous solution contained 4.34 g/liter of $K_2H_2Sb_2O_7$ or calculated as $2 \cdot KSb(OH)_6$ – 5.24 g/liter. According to Prikhodko's results [2], 2 ml of a saturated aqueous solution of potassium antimonate precipitates 2.97 mg sodium. If it is assumed that the $Sb(OH)_6^-$ ion is precipitated quantitatively as $NaSb(OH)_6$, then the concentration of $KSb(OH)_6$ should be 16.97 g/liter. Other authors [4] recommend that the solution prepared should contain not less than 10 g/liter of $KSb(OH)_6$.

Concentrated aqueous solutions of $KSb(OH)_6$ (20 g/liter) are unstable, become turbid, and an amorphous precipitate is formed. Addition of KOH slows down the decomposition of the reagent, but in the course of several days a crystalline precipitate is formed in addition to the amorphous one. Dilute alkaline solutions can be kept for a longer time, but their use for precipitating sodium followed by addition of alcohol leads to a number of complications.

For a constant alcohol concentration, e.g. 25-30%, the solubility of $KSb(OH)_6$ decreases with increasing KOH, while the sensitivity of the reagent solution decreases. As a result it is essential to avoid a large excess of KOH. It is sufficient to add 0.3-0.5 g/liter of KOH to the solution of antimonate to suppress its hydrolysis.

If one takes into account the decrease in concentration of $KSb(OH)_6$ as a result of dilution on adding the reagent to a solution of alkaline salts (1 ml test solution + 4-5 ml reagent), then the following solution may be recommended for determining small amounts of sodium in the presence of 40-50 mg KCl: for the determination of sodium in a 25% alcoholic medium[1], 4.5-4.6 g/liter of $KSb(OH)_6$, 0.3-0.5 g/liter of KOH, 25-26% ethyl alcohol (Reagent 1); for the precipitation of sodium in 30% alcoholic media, 2.7-2.8 g/liter $KSb(OH)_6$, 31-32% ethyl alcohol and approximately 0.3 g/liter KOH (Reagent 2). These solutions of $KSb(OH)_6$ do not hydrolyze and can be kept for a long time.

Quantitative Determination of Sodium in Chemically Pure NaCl and in Mixtures with KCl

Determination of sodium was carried out in centrifuge tubes, well cooled in melting ice, using an iodometric end point. The aliquots of test solution in all cases were 1 ml and consisted of an alcoholic solution of NaCl or of NaCl mixed with KCl. 4-10 ml of precipitant was added to these aliquots, the amount added depending on the amount of sodium present.

Determination of sodium in solutions of chemically pure NaCl by means of the solutions of potassium antimonate recommended above in either 25 or 30% alcoholic media does not present any difficulties. The maximal experimental error in determining 0.1-1.0 mg of sodium does not exceed 6%; the mean arithmetic error is $\pm 3\%$.

Best results are obtained on precipitating sodium in the presence of KCl with Reagent 1 [4.5-4.6 g/liter $KSb(OH)_6$] when the total concentration of alcohol (salt solution + reagent) is within the limits 24-25%. The salt solution NaCl + KCl should contain 20% alcohol.

Repeatable results are obtained for 0.4 mg sodium. Low concentrations of sodium (less than 0.3 mg) are not precipitated completely in the presence of KCl. Vigorous rubbing of the test tube walls with a glass rod and prolonged cooling can sometimes effect precipitation of $KSb(OH)_6$ as needles even when sodium precipitation is incomplete.

Results of determination of sodium in 29-30% alcoholic media with Reagent 2 are given in Table 2.

The minimal amount of sodium which can be determined in the presence of 40 mg KCl in 29-30% alcoholic media is 0.2 mg. The relative error does not exceed 5%.

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1) Alcohol concentration is expressed in % by volume without taking contraction on mixing into consideration.

TABLE 1

Determination of Sodium in the Presence of Potassium Chloride in 24-25% Alcohol in Water

Amount taken, in mg		K:Na	Amount of reagent, in ml	Sodium found		Mean value, in %
Sodium	KCl			in mg	in %	
0.1	40	209.8	5	0.07	70.0	115.0
	40		5	0.16	160.0	
0.2	40	104.9	5	0.135	67.5	78.3
	40		5	0.178	89.0	
0.3	40	69.9	5	0.316	105.3	100.8
	40		5	0.289	96.3	
0.4	40	52.3	5	0.412	103.0	103.8
	40		5	0.418	104.5	
0.5	40	42.0	5	0.499	99.8	101.6
	40		5	0.517	103.4	
2.0	40	10.5	10	1.990	99.5	99.5
3.0	40	7.0	10	2.956	98.5	98.5

TABLE 2

Determination of Sodium in 29-30% Alcoholic Media in Mixtures with KCl

Amount taken, in mg		K:Na	Amount of reagent, in ml	Sodium found		Mean value, in %
Sodium	KCl			in mg	in %	
0.1	40	209.8	4	0.170	170.0	
			4	0.076	76.0	123.0
0.2	40	104.9	4	0.209	104.5	
			4	0.209	104.5	104.5
0.3	40	69.9	4	0.309	103.0	
			4	0.298	99.3	101.2
0.4	40	52.5	5	0.409	102.3	
			5	0.420	105.0	103.7
0.5	40	42.0	5	0.510	102.0	
			5	0.500	100.0	101.0
1.0	40	21.0	7	0.999	99.9	
			7	0.988	98.8	99.4

Determination of Sodium in Natural Products

A solution of $KSb(OH)_6$ gives precipitates with almost all cations with the exception of potassium and small amounts of NH_4^+; for determination of sodium in natural products therefore, it is necessary to separate total chlorides without contamination from other elements.

We carried out sodium determinations in plants, water, in stomach secretions and in waste from food processing factories. Experiment showed that the mixture of sodium and potassium chlorides separated usually contained a small amount of alkaline-earth metals and magnesium. These contaminants at low sodium

concentrations in the mixtures give a turbidity with potassium antimonate and an amorphous precipitate is formed[1].

For complete removal of these interfering elements, a mixture of the following composition was used:

Water	72 ml
Saturated solution of ammonium carbonate in ammonia[2]	2 ml (no more)
10% Ammonia	5 ml
2% Alcoholic solution of o-hydroxyquinoline	5 ml
Ethyl alcohol	16 ml

When the sodium and potassium chlorides have been dissolved in the ammonia-hydroxyquinoline solution described, the solution is transferred to a centrifuge tube, and the whole heated to 60°. After cooling, the precipitate formed is centrifuged and the sodium can be determined in the transparent solution. Control tests on sodium mixed with KCl solution containing o-hydroxyquinoline, ammonium carbonate and ammonia at the same concentrations as in the mixtures adduced above gave results of the same accuracy as for determination of sodium in alcoholic solutions of NaCl + KCl.

It is thus possible to determine sodium quantitatively in the presence of 40 mg KCl in ammonia-hydroxyquinoline media in 12-15 ml centrifuge tubes: in 24-25% alcoholic media; 0.4-3.5 mg, in 29-30% alcoholic media, 0.2-1.5 mg. In the first case the maximal ratio of K:Na is 52, while in the second case it is 105.

Determination of Sodium

1. Alcoholic Solution of Potassium Antimonate. The commercial product often contains various contaminants: nitrates, free alkali, etc. In the presence of these contaminants, it is very difficult to establish the concentration of $KSb(OH)_6$ in solution by iodometric titration. Purification of the commercial product is therefore essential.

To 30-40 g of $KSb(OH)_6$ is added 100 ml distilled water (10-15°) and the whole thoroughly stirred 3-4 times in the course of 20-30 minutes. The precipitate is washed twice with cold distilled water, the water being removed by decantation. It is then washed two or three times more with distilled water under suction. The purified preparation is then dried between filter papers.

500 ml of distilled water is heated in a 1000 ml Pyrex flask to the boiling point, when 3.5 g of purified $KSb(OH)_6$ is added in small amounts and the mixture boiled for 3-4 minutes (no more). The flask is cooled under the tap and 3.5-4 ml of 10% KOH added. 185 ml of 96% ethyl alcohol is then gradually added with stirring. After 24 hours the mixture is cooled for 2-3 hours in melting ice, and the precipitate filtered through an ashless filter paper under suction. The concentration of $KSb(OH)_6$ in solution is checked by iodometric titration in a strongly acid medium (10-15% HCl). Calculations are based on the following equations:

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1) Magnesium gives a crystalline precipitate.

2) This solution is prepared by passing CO_2 generated from a Kipp through some wash water into a cooled ammonia solution until insoluble crystals form.

$$KSb(OH)_6 + 6HCl + 2KI = 3KCl + SbCl_3 + I_2 + 6H_2O;$$

$$I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

2-3 ml of $KSb(OH)_6$ solution are used for titration.

If the $KSb(OH)_6$ concentration is greater than 4.5-4.6 g/liter, the solution is diluted with 25.5% alcohol.

In order to determine sodium in a 30% alcoholic medium the reagent should contain 31-32% alcohol, 2.7-2.8 g/liter $KSb(OH)_6$ and ca. 0.3 g/liter KOH. A solution of this concentration is prepared by dilution of the concentrated solution. Solutions of potassium antimonate should be stored in a pyrex flask or in a flask coated with paraffin wax.

2. Concentrated HCl. Hydrochloric acid almost invariably leads to separation of traces of iodine during iodometric titration (because of its free chlorine content).

This separation of iodine can be prevented by addition of the requisite amount of sodium thiosulfate to the hydrochloric acid. 10 ml of water is added to each 100 ml of the concentrated hydrochloric acid prepared for iodometric titration and the solution thus obtained used for dissolving the precipitate.

Analytical Procedure. The chlorides of the alkali metals, separated by any suitable method, at a ratio of K:Na $\leq$ 100, are dissolved in the exact volume of freshly prepared ammonia-hydroxyquinoline mixture (see above) so that the total amount of salts does not exceed 40-45 mg/ml and the amount of sodium should be within the limits of 0.2-3.5 mg. The beaker or flask used should be covered to decrease evaporation of solvent.

The salt solution is poured into dry test tubes, which are stoppered with corks and stood for 5-10 minutes in a warm water bath (50-60°). They are then stood for 1 hour at room temperature before centrifuging. The transparent filtrate which has a yellow tinge (excess of o-hydroxyquinoline) is poured into some more dry test tubes which are stoppered with rubber bungs and left to stand in the dark until aliquots are taken for sodium determinations. Decomposition of o-hydroxyquinoline on keeping the solution of salt mixture for several days has no effect on the analytical results.

1 ml aliquots of the ammonia-hydroxyquinoline solution of the mixture of NaCl + KCl are transferred to centrifuge tubes and in accordance with the amount of sodium taken, dilute or concentrated reagent is added. For amounts of sodium equal to 0.5-3.5 mg, initially 5 ml of concentrated reagent solution is added (T = 4.6 g/liter) and then after 10-15 minutes, according to the amount of precipitate, another 2-5 ml of the reagent is added, etc. To test tubes containing small amounts of sodium (0.2-0.6 mg) initially only 4 ml of dilute reagent (T = 2.8 g/liter) is added, and then after 10-15 minutes, according to the amount of precipitate formed, 1-3 ml is added. No reagents are added to tubes in which there is no precipitate, or it is doubtful that any has formed.

If the amount of sodium is not known, then a qualitative determination is carried out first. In order to do this, the following procedure is adopted: 4-5 ml of concentrated reagent is added to 1 ml of the test solution which is then kept under observation for 3-5 minutes. If an appreciable amount of precipitate forms, then subsequent determination of sodium should be carried out in a 25% alcoholic solution with the concentrated reagent. If no precipitate forms, or only an inappreciable amount, then the dilute reagent is used (T = 2.8 g/liter). As soon as reagent has been added, the test tubes are stood for 3-4 minutes in melting ice or snow for a preliminary cooling, the contents of the test tubes are thoroughly mixed with a glass road, the rod is grazed slightly on the sides of the tube and rinsed with 4-5 drops of 35% alcohol, and the tube left to stand for a further hour in the ice.

Preliminary cooling is essential in order to get coarse crystals of $NaSb(OH)_6$. Rapid cooling when there is a relatively large amount of sodium present leads to the formation of fine crystals.

While the test tubes are being cooled in ice, the 35% alcohol solution to be used for washing is also cooled in the same way. After an hour the precipitate which is not firmly attached to the test tube walls is displaced by means of a glass rod and centrifuged. The liquid + precipitate are sucked off with a bulb pipet. If crystals appear in the liquid then they are centrifuged out once again, etc. After removal of reagent, test tube and precipitate are stood in the ice bath.

The precipitate is washed with cooled 35% alcohol. The total volume of wash liquor for the first washing should be 1-2 ml. The tubes are centrifuged for 1-2 minutes. The wash liquor is sucked off, the test tubes cooled, and the precipitate washed again twice. The last two washings should be made with a smaller volume of 35% alcohol. The temperature of the wash liquor should not be greater than 2°.

The washed precipitate is dissolved in 6 ml of the special concentrated hydrochloric acid which does not liberate iodine. The solution is transferred to a narrow necked 50-100 ml conical flask, the test tube is rinsed 3 times with pure distilled water (3 ml of water each time), 1 ml of freshly prepared 10% potassium iodide solution is then added, and after 3 minutes, the whole is titrated with 0.025 N thiosulfate solution from a micro-buret to a weak yellow color. 1-2 drops of 0.5% starch solution is added, and the titration finished off.

For a ratio of K:Na > 100, excess KCl is preliminarily removed from the mixture of NaCl and KCl. This operation was carried out by a modification of Vinogradov and Dundur's method [1].

The mixture of NaCl and KCl is dissolved in 2 ml water and transferred to a 25 ml standard flask. The flask or beaker containing the original dry salts is rinsed first with 1 ml water to which has been added 3-4 ml of 96% ethyl alcohol, and then with alcohol only a few times. The solution is shaken and after cooling to 20°, the volume is made up to the mark with alcohol. It is then allowed to stand for 1 hour. The alcoholic solution is centrifuged and the centrifugate poured into a dry test tube (flask) from which exactly 15-20 ml of solution is taken and evaporated to dryness. The dry residue is dissolved in an exactly measured volume of the ammonia-hydroxyquinoline mixture, and further operations carried out as described above.

If during separation of excess KCl in the 25 ml flask, a large amount of precipitate is formed, then a correction for the volume of precipitate must be applied. It can be taken as a rough approximation that 1 g of precipitate has a volume of 0.5 ml; the amount of NaCl + KCl in alcoholic solution is 0.120-0.150 g. 0.15 g is therefore subtracted from the total chlorides, and the remainder divided by 2. The results obtained are the volume of precipitate which is subtracted from 25 ml.

For a ratio of K:Na $\leq$100, sodium can be determined in the presence of other salts (not chlorides) as long as all the cations with the exception of potassium and sodium are removed. In such a case the solubility of the dry salts should be sufficient for getting them into solution on treatment with ammonia-hydroxyquinoline mixture.

E.g., determination of sodium can be carried out as follows: The dry residue obtained from a definite volume of water is treated simultaneously with solutions of ammonia, ammonium carbonate, and o-hydroxyquinoline. The filtrate is evaporated to dryness after removal of the precipitate, the residue is calcined at 500° (for removal of ammonium salts) and then dissolved in the ammonia-hydroxyquinoline mixture. Subsequent procedure is the same as for determination of sodium in chloride salts.

If only the ammonia-hydroxyquinoline mixture need be used for removal of contaminants contained in the dry residue from the water, then there is no need to carry out a preliminary treatment of the dry salts.

SUMMARY

1. By means of a micro method which has been developed, it is possible to determine sodium as antimonate in the presence of large amounts of potassium.

Determination of sodium in 24-25% alcoholic media is accurate enough for a ratio of K:Na $\leq$ 50.

When 30% alcoholic media are used, it is possible to determine sodium at a ratio of K:Na of $\leq$ 100.

For a ratio of K:Na $>$ 100 it is possible to remove excess KCl with ethyl alcohol.

The mean arithmetic error for the determination of 0.2-3 mg sodium is ca. 3%.

2. The use of mixtures of solutions of ammonia, ammonium carbonate, and o-hydroxyquinoline and ethyl alcohol for removal of contamination present in sodium and potassium salts permits determination of sodium not only in ash from plant material but in other natural objects as well.

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THE APPLICATION OF MATHEMATICAL STATISTICS IN ANALYTICAL CHEMISTRY[1)]

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Articles have started to appear recently in our analytical journals which have been devoted to the application of mathematical statistics in analytical chemistry, in which the advantages of this important branch of mathematics have been clearly demonstrated, and recommendations made for its application in evaluating control methods in technics. A number of actual questions in the practical application of mathematical statistics under the conditions of control work in factory laboratories has also been posed.

E.g., Gracheva [1] has put forward a formula for calculating errors and permissible errors in analytical results, and also a rule for excluding 'freak' errors from a series of results. This material is however not illustrated by actual examples.

The application of mathematical statistics is most fully treated in Komar's article [2], where the theoretical basis of this method is given, in addition to derivation and use of formulas together with actual examples of the use of the method in treating analytical results.

We are in full agreement with Komar's approach and the method he has recommended for laying out results.

Komar proposes, without adducing tables of results, to characterize the method by the following indices:

1) n – the number of analyses;

2) σ^2 and S^2 - the dispersion of an individual result and of the arithmetic mean;

3) $\epsilon_\alpha = t_\alpha \cdot S_x$ – the accuracy for a given confidence α;

4) the relation between dispersion and the initial concentration of the test material;

5) the relation between dispersion and the concentration of other materials.

It is however possible to detect systematic errors by a simpler method than that proposed by Komar. This is based on a comparison of the means of two series of analyses.

If there are no systematic errors, then it can be assumed that the means of two series of analyses are the approximate values of the same value E (mathematical expectation):

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1) Occasioned by N. P. Komar's article in J. Anal. Chem., 7, 325 (1952). [See Consultants Bureau Translation, page 361.]

if $\bar{x}_1 \approx E$ and $\bar{x}_2 \approx E$

($\bar{x}_1$ is the arithmetic mean of the first series of analyses, $\bar{x}_2$ the arithmetic mean of the second series of analyses), then $\bar{x}_1 \approx \bar{x}_2$.

The actual amount of material lies within the limits $E \pm \epsilon_\alpha$, where ϵ_α is the accuracy which is equal to $\tau_\alpha \cdot S_{\bar{x}}$.

A difference between $\bar{x}_1$ and $\bar{x}_2$ which is greater than ϵ_α indicates a displacement in the mathematical expectation, i.e., indicates the existence of a systematic error. Thus, if we consider Zolotukhin's results on the determination of beryllium as adduced in Komar's article, the presence of a systematic error can be established as follows:

If we accept as the true value one of 2.6550 mg/equivalent of beryllium which is the mean of a number of irreproachable results and then calculate the difference between this value and the value obtained by Zolotukhin's method, 2.6465 mg/equivalent, we get –

$$2.6550 - 2.6465 = 0.0085 = 8.5 \cdot 10^{-3} \text{ mg/equivalent.}$$

This difference is greater than the accuracy $\epsilon_\alpha = \pm 8.2 \cdot 10^{-3}$, thus indicating the existence of a systematic error. It is obvious that this method cannot be recommended for the analyses of large numbers of samples. Komar also treats the results of Golubtsova's method of determining niobium statistically; in this case for 11 replicates no systematic error could be found.

In some cases, systematic errors can be detected without recourse to calculation simply on the basis of the signs of the deviation of the results obtained from the true content. Since positive and negative values of random errors are of equal probability, then a sudden increase in the number of errors of the same sign points immediately to a systematic error. E.g., as in the determination of tin with the reagent "anthrazo" proposed in 1945 by V. I. Kuznetsov.

One of the most important questions in analytical chemistry is the number of replicates necessary to give reliable results, since it is obvious that the most valuable method is the one which requires the least number of replicates to ensure a guaranteed accuracy.

This number can be calculated by means of a formula as shown in Komar's article. It is also possible to treat statistically two series of analytical results with different n.

V. A. Zolotavin recommends an in situ method for the determination of vanadium in ferrous alloys. In carrying out his determinations, Zolotavin made no less than six replicates from which he drew positive results. A statistical treatment of his tabulated results shows fewer determinations, e.g., four, would have been insufficient since the accuracy is not within the permitted limits. E.g., if we consider series b of the analytical results in Table 1 adduced by Zolotavin, this series contains results which are closest together, the accuracy (see table) is ±0.035%, i.e., outside the permitted limits of 0.025%. For six determinations (series b, Table 2), the accuracy, which is ±0.023%, is within the permitted limits.

On the basis of these results Zolotavin should have concluded that the irregularities in dissolving test material in the in situ method of determining vanadium by his method evened out when 6 analyses were made, and he should have recommended that this number of analyses should be carried out.

If the "true" content of test element is known, then there is no need to use the cumbrous mathematical apparatus proposed by Komar for an arithmetical treatment of the results.

Statistical methods should be used when the "true" content of material is unknown, i.e., when there are no assay methods which can be used to give satisfactory results for comparison with the results obtained by the test method. E.g., arbitrary analytical characteristics of the type of the "oxidizability" of water, and the yield of volatile materials and coke in coal are assay methods of this type. They are useful for the study of redox potentials, for the study of the conditions under which reactions are best carried out when the mechanism is unknown, etc.

Tables of Results Obtained by V. L. Zolotavin
for the Determination of Vanadium by an in situ Method

(Vanadium content 0.58%)

Series b, Table 1

1	0.56
2	0.56
3	0.61
4	0.57
Mean	0.575

For 4 replicates:
$\Delta = 0.0175$
$\sigma_{\bar{x}} = 0.0220$
$S_{\bar{x}} = 0.0110$
$\epsilon_{\alpha} = 0.0350$

for a confidence of 0.950 and
$n = 4$; $\tau_{\alpha} = 3.18$

Series b, Table 2

1	0.62
2	0.53
3	0.59
4	0.58
5	0.58
6	0.58
Mean	0.580

For 6 replicates:
$\Delta = 0.0167$
$\sigma_{\bar{x}} = 0.0208$
$S_{\bar{x}} = 0.0085$
$\epsilon_{\alpha} = 0.0230$
for a confidence of 0.950 and
$n = 6$; $\tau_{\alpha} = 2.57$

Thus, the author of the present article calculated theoretical curves for the relation between the amounts of various oxidizing agents used for oxidizing organic materials in water. In particular, a comparison was made of the results of their oxidizability by permanganate and the "use of oxygen dissolved in the water." Complex curves were obtained which do not bring out the real relation. On the basis of these results, it was concluded that the existing methods of determination do not characterize the amount or the composition of the organic material in the water and require reexamination.

In studying methods of determining components, the "true" content of which can be established by other methods, there is no need to calculate graphical relations for establishing correlating formal relations between various factors. In these cases it is possible to determine experimentally a functional connection between the separate factors and the accuracy of analysis.

Mathematical statistics permits a correct evaluation of analytical methods and helps to plan future study and development. The application of statistical methods should be studied by analysts in all cases when practical necessity requires it. Mathematical statistics cannot replace experiment and is not an end in itself.

Received October 22, 1953.

LITERATURE CITED

[1] E. G. Gracheva, J. Anal. Chem., 7, 48 (1952).[1])

[2] N. P. Komar, J. Anal. Chem., 7, 325 (1952).[2])

1) See Consultants Bureau Translation, page 51.
2) See Consultants Bureau Translation, page 361.

DISCUSSION

From the Editorial Board

A Discussion Arising from an Article by M. B. Shchigol and N. B. Burchinskaya entitled "The Quantitative Determination of Trivalent Iron by Means of Tetraborate." [See J. Anal. Chem., 7, 289 (1952)[1], the critical observations made by A. K. Babko, Ibid., 8, 127 (1953)[2], and the answer of Shchigol and Burchinskaya to these criticisms, Ibid., 8, 185 (1953).[3]

The editorial board considers that A. K. Babko's criticism of M. B. Shchigol and N. B. Burchinskaya's article on the method employed by them for studying reactions between $FeCl_3$ and $Na_2B_4O_7$ in aqueous solutions and the conclusions drawn by them, is justified. The authors carried out a potentiometric titration of $FeCl_3$ with $Na_2B_4O_7$ in which they used platinum with platinum black as the electrode. In so far as the latter reacts sensitively to changes in hydrogen ion concentration which inevitably occur during titration, with borax, then the conclusions re complex formation with borate ions in the system considered cannot be regarded as clear cut and therefore, are inconclusive.

Shchigol and Burchinskaya explain the behavior of the electrode in their case, as an oxidation reduction process, on the basis that there is always a small amount of Fe^{2+} ions in solution of trivalent iron, and this small number of Fe^{2+} ions ensures a definite change in the oxidation-reduction potential of the system. This seems rather a far-fetched assumption. Moreover the Fe^{3+}/Fe^{2+} electrode may be sensitive to borate ions and may be no less sensitive to OH^- ions as well. We do not deny the possibility of complex formation in the system $Fe^{3+} - B_4O_7^{2-}$. We are only concerned with the deficiencies of the method employed to decide this question, since the method actually used leads to results which are possible of more than one interpretation. What has just been said is also applicable to the results of cryoscopic measurements of this system where the choice of the direction taken by the curve is somewhat arbitrarily chosen.

We may point out that the formation of complex silver cyanide in the system $AgNO_3 - KCN - H_2O$, where the alkaline media which is always formed in the second stage of the reaction (formation of $[Ag(CN)_2]^-$), would seem to give rise to a side reaction No one, however, has any doubts as to the direction taken by this reaction when one takes into account the relatively high solubility of AgOH on the one hand [which cannot be said about $Fe(OH)_3$], and the very high stability of the ion $[Ag(CN)_2]^-$ ($K_{instability} = 1.10^{-21}$), which, by the way, follows from the shape of the solubility curve of AgCN in KCN solutions (the slope is 45° despite the negligible solubility of AgCN, ca. 10^{-6} mol/liter), and finally, when one takes into account that a silver electrode which is sensitive to just these silver ions can be used in this system.

There is no need here to touch upon other less important aspects of the case under discussion, although perhaps we should refer to the basis of observations made by M. B. Shchigol and Burchinskaya in reference to an unfortunate expression of Babko's, viz., "it is well known that excess of a coordinating ions usually leads to the formation of a more stable complex." When the process of complex formation in a system is stepwise (just the case in point), this sentence of Babko's could be interpreted as meaning that each successive complex is more stable than the preceding one, which naturally Babko is not in a position to confirm. Here, however, we can only refer to the inaccuracy of the sentence; it would be more correct to say that excess of a

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1) See Consultants Bureau Translation, page 325.
2) See Consultants Bureau Translation, page 145.
3) See Consultants Bureau Translation, page 205.

coordinating ion does not form a more stable complex[1]), but only makes any of the complex compounds formed in the given system more stable.

Of greater importance is another fact, viz., the facility with which some authors draw far-reaching conclusions and recommend this or that value of a constant on the basis of rather unsuitable physico-chemical experiments. It is unfortunate that this reproachful practice, which is used for the formal interpretation of experimental results, is rather widespread; particularly when we are trained in our country in a school of chemical analysis according to the precepts of which systems which have complex chemistry should be studied by a number of methods in order to arrive at correct interpretations of the composition of compounds formed in the system on the basis of a study of property-composition diagrams, and in addition, of the composition of solutions not containing solid phases. First of all, it is essential to be sure of the correctness of our qualitative interpretation (composition of the compounds formed), and only when we are sure of this should we carefully consider the quantitative aspect of the case (calculations of constants, etc.).

The editorial board must agree with Shchigol and Burchinskaya that a study of the chemistry of borate compounds in solution is of great interest and deserves attention. The board is quite willing to place the J. Anal. Chem. at the disposal of anyone who wishes to publish work on this question, but with the reservation that from the methodological point of view, the work will be beyond reproach. Shchigol and Burchinskaya's first paper is an exception, though this does not mean that the editorial board shares the opinion of the authors with respect to some of their conclusions.

[1]) Incidentally, the word complex should not interfere with the substitution of the term, complex compound, or complex ion.

IVAN VLADIMIROVICH TANANAEV

(On His Fiftieth Birthday)

On the 4th of June 1954 Ivan Vladimirovich Tananaev, one of the foremost Soviet scientists, a Corresponding Member of the Academy of Sciences, a Stalin prize winner, a professor, and a doctor of chemical sciences, celebrated his fiftieth birthday and his thirtieth year of scientific and teaching activity.

His scientific and practical activity is unusually wide and varied. Tananaev, a talented pupil of N. S. Kurnakov, is well-known as an analytical chemist, an inorganic chemist, a skillful research worker, and a wonderful teacher.

Tananaev finished his course in the Chemical Faculty of the Kiev Polytechnic Institute in 1925 but stayed there in the Analytical Chemistry Department as an assistant and became a candidate for a higher degree. In 1928 he defended his thesis on "The action of oxalic acid on metal fluorides," which he completed under the direction of Prof. N. A. Tananaev, in whose laboratory he worked up to 1934. During this period he developed a number of new analytical methods for production control, including methods of determining potassium, zinc oxide, calcium oxide, calcium fluoride in fluorspar, fluorine in apatites and phosphorites, and tin, lead, antimony, and copper in Babbitt metal, etc.

In 1934 Tananaev moved to Tbilisi, where he worked as director of the Laboratory of the Chemical Institute of the Transcaucasian Branch of the Academy of Sciences. In a comparatively short time (1934-1935) he organized a large number of coworkers and carried out many important investigations. All this work, which can be regarded as the second stage of his scientific work, is characterized by the development of new analytical methods with a wide application of physico-chemical methods for the study of reactions.

Thus, Tananaev in conjunction with his coworkers, proposed tin amalgam for the rapid determination of Fe, Cu, Hg, Sn, Ti, Au, Pt, W, V and Ag; a potentiometric method for the determination of potassium using the ferrocyanides of Co, Ni, Mn and other metals; new adsorption and oxidation-reduction indicators: methyl violet, blue ethyl acid RRB, etc. New methods for the determination of Si, the alkaline metals, Mg, Ca, Al, and Fe as fluorides (fluorimetry) were also developed; and a systematic study was made of the solubility of precipitates and hydrolytic adsorption.

His activity in the Chemical Institute of the Georgia Academy of Sciences and in the Tbilisi Chemico-Technical Institute where he was the head of the chair of Analytical Chemistry, led to many fruitful results. It was during this period that the ground work was laid for the scientific researches which he is still developing at the present time.

His scientific activities reached their peak at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences, where he went in 1935.

In 1939 he successfully defended his thesis for a doctor's degree taking as his subject, "The physico-chemical analysis of fluoride compounds and their application in analytical chemistry." He carried out this work under the direction of N. S. Kurnakov. While still working on his doctorate he studied at the Laboratory of the Institute of General and Inorganic Chemistry in close contact with its director, Prof. B. G. Karpov, after whose death Tananaev became the

head of the laboratory. This laboratory was reorganized in 1948 into a laboratory of the Chemistry and Analysis of Rare Elements. Tananaev is still its director.

During this period Tananaev has been basically occupied with working on a number of problems related to the application of physico-chemical methods to analytical chemistry. In a series of investigations along these lines, Tananaev and coworkers in effect made a field, which had previously only been touched, a special field of analysis. Tananaev proposed a method based on the absorption of light by homogeneous and heterogeneous systems as a new method of physico-chemical analysis. He worked on a number of methodological questions connected with the study of the chemistry of interaction between ions in solution, and also on a number of theoretical questions and new criteria relating to the coefficient of molar extinction of suspensions and finding optimal conditions for turbidimetric analysis. This work was awarded the Kurnakov prize.

Tananaev was the first to adopt the method of measuring precipitate volumes as a physico-chemical method. The vast amount of material accumulated on this question is not only of great practical significance, but also opens up new perspectives for the study of the theory of formation and structure of analytical precipitates. In a series of papers published by Tananaev and coworkers entitled "Physico-Chemical Analysis of Systems of Analytical Importance," the principal results relating to the study of analytical reactions by the methods of light absorption, solubility, measurements of precipitate volume, E.M.F., etc. were laid out. This field has been developed widely in recent years in its application to the study of the chemistry of the rare elements according to a plan which did not have only an analytical slant, but was predominantly from a general and inorganic point of view. Compounds of the following elements were among those studied by Tananaev, et al: Rb, Cs, Be, Ga, In, Tl, Zr, Ge, Nb, Ta, Mo, W, and the rare earths. Tananaev paid particular attention to the fluorides and ferrocyanides of the rare elements. These investigations, which were carried out over a number of years, were distinguished by the care and accuracy with which the experimental part was carried out, accuracy being essential in dealing with such complex subjects. As a result of this work, a number of new compounds were prepared and studied for the first time; these included: $LiF \cdot HF$, $H_3AlF_6 \cdot 6H_2O$, $H_3AlF_6 \cdot 3H_2O$, $H_3FeF_6 \cdot 3H_2O$, $KTaF_6$, $KNbF_6$, $PbSO_4 \cdot 2K_2SO_4$, $K_4Ni_4[Fe(CN)_6]_3$, $5Cd_2[Fe(CN)_6] \cdot 4K_4Fe(CN)_6$, $11NaF \cdot 4FeF_3$, etc. Many of these found practical application. This work enriched the chemistry of salt-equilibrium and indicated new ways of preparing a number of salts on the commercial scale.

Of great importance is the work of Tananaev and his coworkers on the composition of cryolite; the old formula Na_3AlF_6 was shown to be incorrect, and a new formula $11NaF \cdot 4AlF_3$ was suggested. On the basis of this formula, Tananaev developed the "Cryolite" method of determining aluminum in the presence of Fe, Ti, Mo, W, V, Zr, and other elements. Work on the chemistry of fluorine led Tananaev in a similar way to develop a new method of volumetric analysis which he called fluorimetry.

In the course of his scientific work Tananaev and coworkers have carried out about 150 investigations. These investigations have raised the theoretical level and the importance of analytical chemistry in our country whereby a number of problems of contemporary chemistry has been solved, particularly problems connected with the chemistry of rare elements.

He has devoted a considerable amount of his time to teaching. He started teaching in 1925 and at various times has taught at the Kiev Chemico-Technical Institute, Tbilisi Chemico-Technical Institute, the Moscow Institute of Non-Ferrous Metals and Gold, and in the Minsk Polytechnic Institute. At present, he heads the Chemistry Section at the Moscow Engineering-Physical Institute. A characteristic feature of Tananaev is that he carries on research work at all the places he teaches, and attracts a large number of coworkers.

In parallel with his teaching and research work Tananaev directs the studies of pupils for various degrees. At present 23 of his students are candidates for degrees in various parts of the Soviet Union.

He has also played an important part in organizational and social work for many years being in charge of the Branch of the Chemistry of Rare Elements, a deputy director of the Institute of General and Inorganic Chemistry, and a member of the Bureau of the Div. Chem. Sci. USSR Academy of Sciences. From its inception he has been subeditor of the J. Anal. Chem., and editor of the Symposium on Chemistry of the Rare Elements.

He has been awarded the Order of the Red Star (1945), the Red Banner (1949) and the Order of Lenin (1954) for his scientific work. He has been awarded a Stalin prize twice.

This has been only a brief outline of his activities.

His contributions to analytical and general chemistry are considerable and are a new phase in the theory and practice of physico-chemical analysis.

He is at present in his prime.

On his birthday a wide circle of Soviet chemists, fellow workers, and scientists wish him the best of health and many further successes in his fruitful work for the good of our country.

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